

STUDIES ON SELECTIVE OXIDATION OF n-BUTANE TO MALEIC ANHYDRIDE ON V P O CATALYSTS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by
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to the

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

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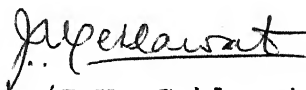
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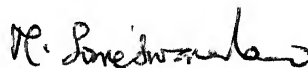
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NOMENCLATURE

B	
B	n-butane
C	Oxides of carbon
C_B	Concentration of n-butane
E	Activation energy
F	Flow rate of reactants
F_B^0	Flow rate of n-butane in the feed
K	Rate constant
MA	Maleic anhydride
p_O	Partial pressure of oxygen
p_{MA}	Partial pressure of maleic anhydride
p_B	Partial pressure of n-butane
p_C	Partial pressure of oxides of carbon
r_B	Rate of reaction of n-butane
r_C	Rate of production of oxides of carbon
r_{MA}	Rate of production of maleic anhydride
s	Standard deviation
T	Temperature
W	Weight of the catalyst bed
X	Conversion of n-butane
Y	Yield of maleic anhydride
Z	Yield of oxides of carbon.
θ_1	Fraction of oxidized sites
θ_2	Fraction of Reduced sites

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SYNOPSIS

Maleic anhydride is an industrially important chemical. In the past, maleic anhydride was produced largely through benzene oxidation. Of recent, its production from oxidation of C₄-hydrocarbons appears commercially more attractive. Vanadium-phosphorous-oxide (VPO) catalysts have been used for these reactions.

In the present study, two types of VPO catalysts were synthesized. One of the catalysts contained iron as a promoter. Both the catalysts had a P/v ratio of 1.2. The catalyst compositions are given below:

Catalyst Composition

Constituents %	V_2O_5	P_2O_5	Fe	Silica gel
Catalyst				
Catalyst A	15.35	9.72	0	74.93
Catalyst B	15.30	9.70	0.5	74.50

The catalysts were characterised by XRD, DTA and TGA analysis. Both the catalysts were found to be thermally stable upto 500°C. They were poorly crystalline and had nearly the same surface area of 58 m²/g.

Experiments were carried out in a fixed-bed tubular reactor to study the effect of contact time, temperature and feed composition on conversion, yield and selectivity with respect to maleic anhydride. External and intraparticle mass transfer limitations were found to be absent.

An optimum temperature of around 375°C gave the best yield of maleic anhydride. At a W/F value of 6 g/(mg mol/s) and at 375°C, the per pass conversion, yield and selectivity respectively were found to be 79.7%, 15.3% and 19.2% for catalyst A and 44.0%, 21.4% and 48.6% for catalyst B. These values are comparable with the work reported in literature (1). The selectivity increased with an increase in contact time but decreased with an increase in the butane concentration in the feed.

Catalyst B containing iron as promoter appears to be promising. Its selectivity with respect to maleic anhydride is much better than the unpromoted catalyst A.

A kinetic model consisting of three different sites on catalyst surface has been proposed. It was found that the formation of maleic anhydride was associated with sites of highest oxidation state and the formation of oxides of carbon was associated with sites of lower oxidation state. Theoretical predictions matched closely with the experimental results. The data reported are likely to be useful for a rational design of industrial reactors. Recommendations for future work have been made.

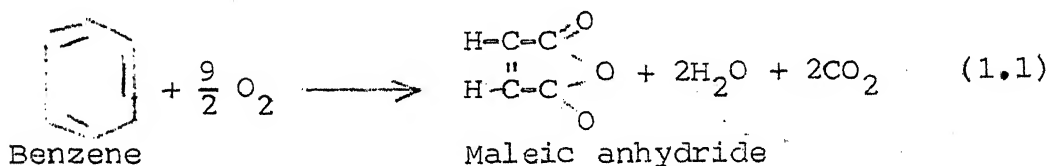
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1. Cavani, F., Centi, G., and Trifiro, F., Appl. Catal., 9, 191 (1984).

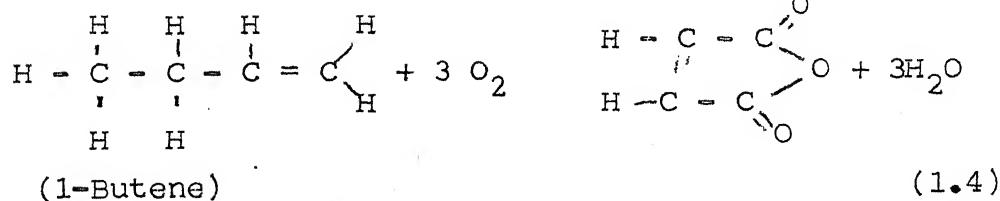
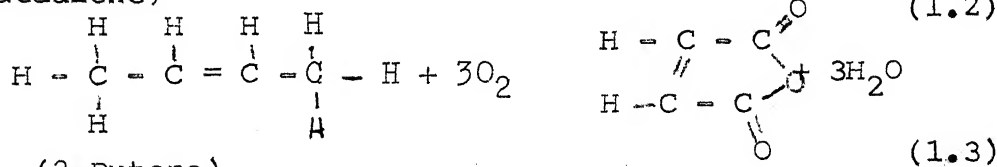
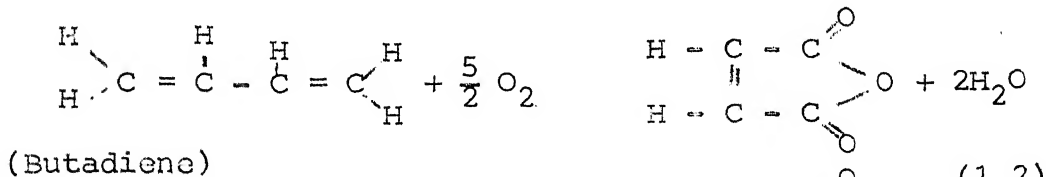
CHAPTER 1

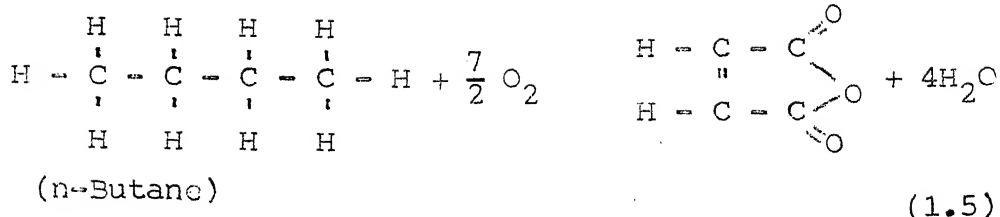
INTRODUCTION

Catalytic oxidation reactions are employed to produce a variety of organic chemicals. Maleic anhydride is an industrially important chemical. It has been produced industrially by the oxidation of benzene (1). The reaction can be represented by:



Maleic anhydride may be produced from the C_4 -feed stock by the following reactions:





During the 1970s a substantial price differential developed between benzene and the C_4 -hydrocarbons (2) and has continued to grow in favour of C_4 -hydrocarbons due to the scarcity of benzene. With this development aided by the stringent controls introduced on benzene emissions from industrial plants, the processes for the production of maleic anhydride based on C_4 -feed stocks appeared economically attractive (3). Consequently, the studies on oxidation of butadiene, butenes and n-butane to produce maleic anhydride gained importance. Of these routes, use of butadiene as a starting material is disadvantageous due to its higher costs. Butadiene is more economically utilized for the production of styrene-butadiene rubbers. Quite understandably, more attention was paid to the oxidation of butene to maleic anhydride (3). Oxidation of n-butane to maleic anhydride has been reported only in a few studies in the literature due perhaps to the low yields obtained in these studies (4,5).

The catalysts described in the literature for oxidation of C-4, hydrocarbons to maleic anhydride are based on Vanadium Phosphorous Oxides (VPO). The mechanistic aspects of the oxidation of butenes on VPO catalysts have been the subject of

several studies. However, only a few publications (6,7) have appeared on the oxidation of n-butane using VPO catalysts.

It is noteworthy that the great potential of several commercial processes based on butane oxidation has been indicated in the literature recently (8,9). For example, the byproduct butane stream from a naphtha cracker or the butane fraction associated with the natural gas may provide an economic alternative to the conventional benzene-route for the production of maleic anhydride. This will be in accordance with the changing industrial trend (10). Under typical Indian conditions, the butane route may prove particularly attractive. in view of the continuing scarcity of benzene and its high costs. Hence, it was considered desirable to undertake a systematic study on the oxidation of n-butane to maleic anhydride using VPO catalysts.

CHAPTER 2

LITERATURE SURVEY AND CHOICE OF CATALYSTS

The production of maleic anhydride may be achieved industrially by oxidation of either benzene or butane-butene streams. As discussed elsewhere, the butane, butene-route may be preferred for future commercial plants (10). The oxidation of butane-butenes has been reviewed by Hucknall (11), Varma and Saraf (12) and by Hodnett (13). The most widely claimed catalysts for this process are based on vanadium-phosphorous oxides. The catalyst composition and methods of preparation have been found to be important parameters in the reaction. Hence, the salient features of the preparation and use of VPO catalysts for the oxidation of C_4 -hydrocarbons are briefly reviewed in the following.

2.1 Effect of Method of Preparation:

Usually, V_2O_5 or NH_4VO_3 is reduced by acids such as hydrochloric acid, oxalic acid, lactic acid etc. in an aqueous medium, or reduced by organic solvents such as methanol, isobutanol etc. with the solvent itself acting as the medium. O-phosphoric acid is added to the reduced solution. Higher BET surface areas are claimed for catalysts prepared in organic media. A comparison of VPO catalysts prepared in aqueous and organic media in C_4 -oxidation to maleic anhydride

by Cavani et al. (14) reveals that the higher surface areas of catalysts made from organic media enable oxidation at lower temperatures.

2.2 Effect of Addition of P_2O_5 to V_2O_5 :

The effect of addition of P_2O_5 to V_2O_5 was first studied by Ai et al. (15-17) for C_4 -olefinic oxidation. It was found that the oxidation activity of the catalysts decreased with increasing P/v ratio although the selectivity increased. Ai et al (15) also studied the activity of V_2O_5 based catalysts towards further oxidation of maleic anhydride. It was noted that at $500^\circ C$, on pure V_2O_5 , 25% maleic anhydride underwent complete oxidation while on P_2O_5 containing catalysts the decomposition was considerably reduced. Apparently, the P_2O_5 content in the catalyst controlled the side reactions in the formation of maleic anhydride.

The activity and selectivity of these catalysts are characterized by the stabilization of the 4 + oxidation state of vanadium due to the presence of phosphorous. Phosphorous is reported to enter the catalyst by solid-state reaction on calcination above $380^\circ C$ with consequent stabilization of the 4 + oxidation state of vanadium (18-20). The stabilization of the oxidation state was further confirmed by Hodnett and Delmon (21, 22) by showing that for catalysts calcined at $500^\circ C$, the reactivity of near-surface regions to reduction by

hydrogen or reoxidation by oxygen were essentially independent of the P/v ratio but the reactivity of the bulk of these catalysts was found to be strongly dependent on the P/v ratio and a slight excess of phosphorous inhibited the mobility of lattice oxygen through the bulk. The catalysts described for n-butane oxidation have been summarised by Hodnett (13). A majority of the patented catalysts have P/v ratios in excess of 1.1. Optimum average valence state was found to be between 4 + and 4.5 + for industrial catalysts (13).

An interesting report about the redox level attained by VPO (P/v = 1) catalysts in a 1.0% butene-air mixture was given by Bordes and Courtine (23). The catalyst was calcined at 750°C in oxygen and nitrogen streams in order to get average valence states of 5+ and 4+ respectively. These catalyst samples were then contacted with hydrocarbon-air feed at 420°C. These samples attained steady-state average valence states of 4.5+ in the case of pre-oxidized samples and 4.3+ in the case of pre-reduced samples. These findings demonstrate the ability of VPO catalyst system to change its solid-state properties depending on the reaction conditions.

2.3 Effect of P/v Ratio on Phase Composition:

The phases encountered in VPO system are numerous. Some of these phases have been tabulated alongwith their principal XRD (X-ray diffraction) spacings by Hodnett (13). The dependence

of phase composition on P/v ratio reported in different studies is presented in Table 2.1. The 'd' spacings from XRD patterns for some of the phases appearing in this table are presented in Table 2.2.

The VPO catalysts activated at low temperatures are often poorly crystalline or amorphous. In such catalysts, the P/v ratio alongwith the reducing agent used in the preparation determines the distribution of vanadium and phosphorous ions within the bulk (13).

2.4 Selectivities of Different VPO Phases:

Selectivities of different VPO phases for C_4 -oxidation towards maleic anhydride are given in Table 2.3. It can be noted that B and β phases, and, a mixture of B phase and α -VOPO₄ are highly selective for maleic anhydride formation. In the case of $(VO)_2P_2O_7$, it cannot be concluded that the high selectivity observed at low conversion will be maintained at near 100% conversion as the selectivity of VPO (P/v = 1) catalysts is known to decrease with decrease in n-butane concentration (29).

2.5 Promoted VPO Catalysts:

Metallic elements can be added to VPO catalysts as promoters in the range of 0.01 to 0.2 atomic ratio of promoter to vanadium to improve activity and selectivity. Some promoters

TABLE 2.1: EFFECT OF P/V RATIO ON PHASE COMPOSITION

P/v ratio	Reducing agent	Precursor	Calcination temp., °C	Final phases	References
< 1	Lactic acid	Amorphous	500	β - VOPO ₄	24, 25
> 1	Lactic acid	Amorphous	500	$\beta^*(V^{4+})$ phase ↓ slow β - VOPO ₄	24, 25
as increases from 1.03 to 1.10	Lactic acid	Amorphous	500	β^* phase is more stable against oxidation to β - VOPO ₄	24, 25
0.95 - 1.10	Lactic acid	Amorphous	650	β - VOPO ₄ is the main product but β - phase is present when P/v < 1	24, 25
Range studied 0.9-1.4	HCl	(VO) ₂ P ₂ O ₇ · 2H ₂ O	380 vacuum	When P/v > 1 β - phase is exclusive, but when P/v < 1 β - VOPO ₄ is present	19, 20, 26, 27, 28, 14
Range studied 0.5-2.0	HCl	-	-	V ₂ O ₅ , V(PO ₃) ₃ & VO(PO ₃) ₂ outside the range; VOPO ₄ , β - VOPO ₄ & (VO) ₂ P ₂ O ₇ within the range.	23

TABLE 2.2: THE 'd' SPACINGS OF DIFFERENT VPO PHASES (13)

Phase	Principal 'd' values
β - VOPO_4	3.48, 3.40, 3.07
α - VOPO_4	3.57, 3.07, 3.01
$(\text{VO})_2 \text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ or the α -phase	5.64, 4.51, 3.66, 2.94
$(\text{VO})_2 \text{P}_2\text{O}_7$	3.87, 3.14, 2.99
β -phase	3.90, 3.13, 2.98
β -phase	3.87, 3.14, 2.98
β^* -phase	4.67, 4.07, 3.14, 2.59
$\text{VO}(\text{PO}_3)_2$	3.97, 3.88, 3.22, 2.47, 2.03

TABLE 2.3: SELECTIVITIES OF DIFFERENT VPO PHASES

Phase	Feed	Temp., °C	Selectivity(S) & Conversion(C)	Ref.
B or β -phases	0.7% C_4H_8 in air	400 - 430	50% S 100% C	14
α -VOPO ₄	0.7% C_4H_8 in air	360	40% S 100% C	14
Mixture of β -phases & α -VOPO ₄	0.7% C_4H_8 in air	380	50% S 100% C	14
β -VOPO ₄	1.5% C_4H_{10} 9.0% O ₂	475	23% S 10% C	30*
(VO) ₂ P ₂ O ₇	1.5% C_4H_{10} 9.0% O ₂	475	63% S 10% C	30*

*Calculated from figures

include Fe, Cr, Bi, Zn, Ti, Zr, Sb etc. A host of patented catalysts (promoted) have been compared by Hodnett (13).

The best results lie around 50-60% yield at 100% conversion.

A recent patent claims 63.7% yield of maleic anhydride for an iron-promoted catalyst $[(V_{0.9} Fe_{0.1}O)_2 P_2O_7]$ against 59.3% for an unpromoted catalyst $[(VO)_2 P_2O_7]$ at 480°C (31).

2.6 Studies on Oxidation of n-Butane to Maleic Anhydride:

Direct oxidation of n-butane to maleic anhydride was first examined by Agasiev et al. (4) on Co-Mo-O and V-Mo-O catalyst systems in the temperature range of 420-500°C. The best results were obtained by a V-Mo-O catalyst, but the yield was only 18 wt.%. Later on, a complex catalyst consisting cerium chloride and Co-Mo oxides supported on silica was developed (5). Butane was first dehydrogenated to butenes which were further oxidized to maleic anhydride by Co-Mo oxides. In this process a higher yield of maleic anhydride (29.8 wt.%) was realised at 490°C. The oxidation of $C_8H_{16}O_{0.5}P_2Mo_{12}O_{40} + 2VO^{2+}$ catalyst was studied but the selectivity towards maleic anhydride was low.

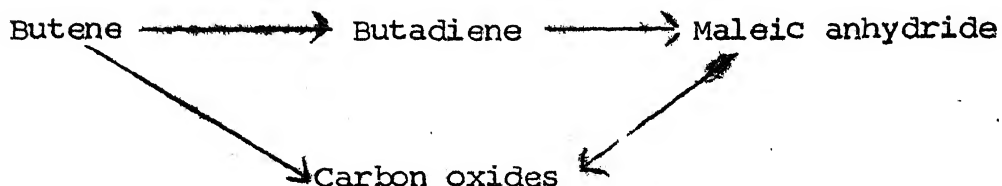
Recent studies on this reaction are related to the VPO catalyst system. Hodnett et al. studied VPO catalysts with P/V ratios in the range 1-10 at temperatures between 380 and 400°C. The yield of maleic anhydride increased with increase in the P/V ratio.

their studies. The catalyst with the lowest P/v ratio was composed of β -VPO₄ (average valence state of +5) whereas the catalyst with the highest P/v ratio was composed of β^* phase (average valence state of +4). Low average valence values, i.e. higher P/v ratios, resulted in higher selectivities. However, for the catalysts containing the B-phase, a deficiency of phosphorous with respect to the P/v ratio of 1.0 increased the maleic anhydride decomposition and an excess of phosphorous reduced the decomposition of maleic anhydride but both the activity and the selectivity were also reduced (33).

The VPO catalysts with P/v ratios in the range of 0.94 - 1.10 were studied for n-butane oxidation by Hodnett and Delmon (25) at 400°C where changes in the bulk composition of the catalysts were minimal. Catalysts prereduced in hydrogen showed greater activity. The selectivities were either found to be constant or increased upon prereduction. Effectively, higher yields at higher conversions were observed. Further, these authors (34-36) suggested that the catalysts with maximum activity and selectivity are constituted of oxidized surface layers built upon VPO reduced core similar to the model proposed by Centi et al. (37) who found increased selectivity with increase in the concentration of n-butane. It was concluded that the selectivity was governed by the amount of surface oxygen available in the vicinity of the adsorption site (29.33).

2.7 Studies on Kinetics and Mechanism of C₄- Oxidation on VPO Catalysts:

Varma and Saraf (39) have found that the redox mechanism first proposed by Mars and Van Krevelen (40) fitted their data in the oxidation of n-butenes to maleic anhydride on a VPO catalyst. Butadiene was found to be the major intermediate in the proposed reaction scheme:



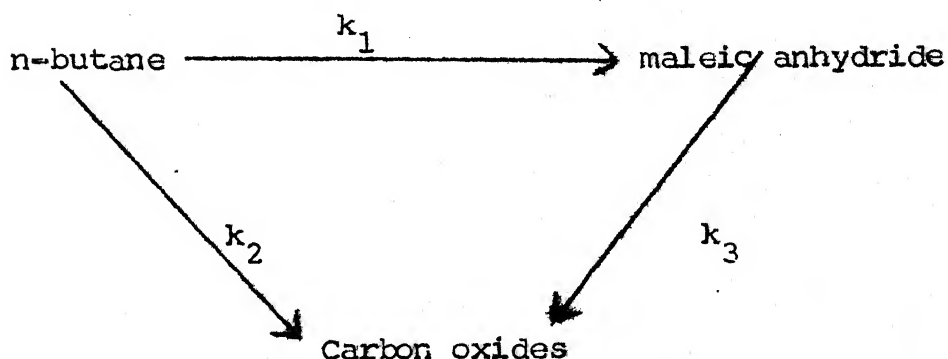
Pseudo-first order rate expressions were fitted to each of the above reaction steps at low hydrocarbon concentrations in air.

A recent study by Cavani et al. (41) revealed two redox couples operating in the oxidation of 1-butene to maleic anhydride. According to these authors, 1-butene adsorbed on a V(IV) site oxidizes to butadiene accompanying the formation of V(III) site. If the concentration of V(V) sites around the adsorbed butadiene is high enough, it is further oxidized to maleic anhydride or carbon oxides. On the other hand, if the concentration of V(V) sites is low, butadiene desorbs from the V(III) site.

In the case of n-butane oxidation, the likely intermediates such as butenes, butadiene etc. were not detected in reactors

operating at low butane concentrations. However, at high concentrations of n-butane Centi et al. (42) detected butenes and butadiene. This behaviour was explained in terms of surface oxygen available for further oxidation of the intermediates. At high concentrations of hydrocarbon, the catalyst is in a much reduced state leaving the scope for the intermediates to desorb from the catalyst surface. As in the case of 1-butene oxidation, a redox couple was proposed to be operating in this reaction scheme. n-butane adsorbed on a V(IV) site converts to olefins accompanying the formation of a V(III) site. Again, if the density of oxidized sites V(V) in the vicinity of adsorbed olefins is high, these olefins are further oxidized to maleic anhydride or carbon oxides. But, if the density of V(V) sites is low, the olefins desorb.

The reaction scheme for the oxidation of n-butane described by Escordino (43) and, Wohlfahrt and Hoffmann (44) is given below:



At low hydrocarbon concentrations, the kinetics was described by three single pseudo-first order rate expressions (43). At extended range of concentrations, rate equations of the following type were reported to fit the experimental data (44). Oxidation of butane is given by

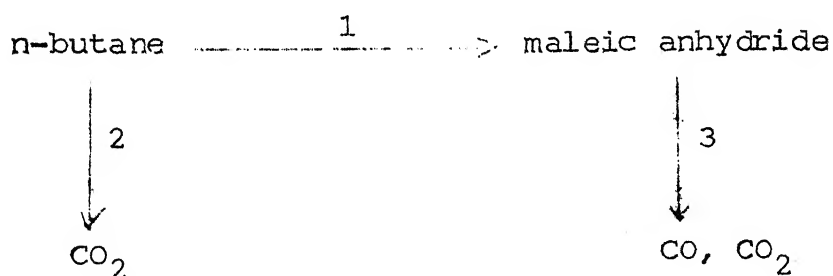
$$r_B = \frac{k p_B p_O^{0.285}}{(1 + K p_B)} \quad (2.1)$$

Maleic anhydride decomposition is given by

$$r_{MA} = \frac{k p_{MA} p_O^{0.285}}{(1 + K p_B)} \quad (2.2)$$

where the subscripts B, MA and O correspond to butane, maleic anhydride and oxygen respectively.

A more recent study by Centi et al. (45) presents a slightly different reaction scheme, which is given by



Rate equations of the following type were given for the three reactions:

$$r_1 = \frac{k_1 K_B p_B p_O^a}{(1 + K_B p_B)} \quad (2.3)$$

$$r_2 = k_2 p_O^b \quad (2.4)$$

$$r_3 = k_3 p_{MA} \frac{p_O^c}{p_B^d} \quad (2.5)$$

2.8 n-Butane Oxidation as Described in Patents:

Several patents claim good yields of maleic anhydride. One of these employs a recycle reactor in which unconverted butane is recycled to improve the conversion and selectivity (46). This reactor is operated with a VPO catalyst at a temperature of 371-427°C and a pressure of 1.27 - 1.75 ~~kg~~ kg/cm² with a 2.0 - 3.5% butane content in the feed stream. In another case (47) butane stream was diluted with propane to keep VPO catalyst activity at higher levels. A 1.5% mixture (50/50) of butane and propane in air was fed over the catalyst at 377°C to get 81% conversion with 69% selectivity. The use of cooling coils below the catalyst bed within the reactor were suggested (48) to cool the product stream to a temperature less than 357°C to achieve improvement in the yield. The improvement was attributed to lesser decomposition of butane.

2.9 Choice of Catalysts for the Present Study:

The foregoing literature survey clearly indicates that the most active and selective catalysts for n-butane oxidation are limited to the VPO system. Most of the studies involved catalysts with P/v ratios very close to unity. In the present

study a P/v ratio higher than unity was selected in order to gain further insight into the role of P/v ratio. Iron has been considered to be an effective promoter. Hence, a second catalyst containing iron in a suitable proportion was also prepared. Both the catalysts were supported on silica gel in order to obtain high surface areas which facilitate the reaction to proceed at low temperatures.

The VPO catalysts with and without an Fe promoter were prepared and characterised using standard techniques. A systematic study for the oxidation of n-butane to maleic anhydride was therefore undertaken.

CHAPTER 3

MATERIALS, CATALYST PREPARATION AND EXPERIMENTAL PROCEDURE

3.1 Materials:

Gases:

Air and n-butane were used in this study. Air from an oil-free compressor - receiver tank was passed through a series of tubes containing calcium chloride, sodium hydroxide and activated charcoal to remove moisture, carbon dioxide and hydrocarbon impurities respectively. C.P. grade n-butane was obtained from M/S Matheson Gas Company, East Rutherford, N.J., U.S.A. which had a reported purity of 99.0 mol% minimum.

Chemicals:

Ammonium metavanadate, oxalic acid, o-phosphoric acid, ferric nitrate and silica gel were used in the preparation of catalysts. Analytical grade ammonium metavanadate obtained from Renal, Budapest, Hungary had a reported purity of 99.5 wt%. Oxalic acid with a reported purity of 99.5 wt% and silica gel were obtained from Sarabhai M. Chemicals Pvt. Ltd., Baroda. Ferric nitrate with a reported purity of 99.0 wt% was obtained from IDPL, Hyderabad. High purity O-phosphoric acid was supplied by E. Merck (India) Pvt. Ltd., Bombay.

3.2 Preparation of Catalysts:

Two silica gel supported VPO catalysts, hereinafter designated as catalysts A and B, were prepared in an aqueous medium as follows.

For catalyst A, 9.64 g of ammonium metavanadate (NH_4VO_3) was placed in 200 ml of distilled water to which 25 g of oxalic acid was added. The mixture was refluxed till the vanadium was reduced to a tetravalent state as indicated by the formation of a clear blue solution. To this solution 5.55 ml of O-phosphoric acid (sp. gr. 1.71) was added. Catalyst A was prepared by adding 36.6 g of -18+25 silica gel to the above VPO solution. The contents were first dried in vacuum at 70°C for 24 h and later at 125°C for 16 h.

Catalyst B was prepared by dissolving 1.66 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in the VPO solution prepared as described earlier prior to adding 36.6 g of -18+25 silica gel. The drying procedure was the same as for the preparation of catalyst A. The catalysts were characterized as per procedure described elsewhere. Table 3.1 gives the catalyst compositions.

The catalyst A had a phosphorous to vanadium (P/v) ratio of 1.2/1.0 and catalyst B had a P/v to iron (P/v/Fe) ratio of 1.2/1.0/0.05. Both the above catalysts were activated in a flow (1125 cc/min) of air at 400°C for 6 h in the experimental reactor.

TABLE 3.1: COMPOSITIONS OF CATALYSTS

Constituents	V_2O_5	P_2O_5 (weight%)	Fe	Silica gel
Catalyst A	15.35	9.72	0	74.93
Catalyst B	15.30	9.70	0.50	74.50

3.3 Experimental Set-up:

A schematic diagram of the experimental set-up is shown in Fig.3.1.

Compressed air and n-butane streams were mixed and passed on to the reactor through a preheater. The preheater was made from a 3 mm stainless steel tubing wound around the top portion of the reactor. The reactor consisted of a 316 grade stainless steel tube of 10 mm I.D. and 300 mm length. The reactor was heated using an electric coil wound around the reactor and properly insulated. The temperature of the reactor was controlled to within $\pm 2^{\circ}\text{C}$. Chromel-alumel axial thermocouples (TC_1) and (TC_2) were used to monitor the temperature of the reactor at the inlet and outlet points.

Beds of calcium chloride and sodium hydroxide were provided in the air-line to remove moisture and carbon dioxide respectively. Another calcium chloride bed was used in the product-line to remove moisture in the product gases. The needle valves V_1 , V_2 and the capillary flow-meters in the n-butane-line and the air-line helped to regulate and monitor the flow-rates. Maleic anhydride formed during the reaction was condensed from the reactor effluents using a glass condenser (cooled by tap water). Gas samples could be collected from the sampling ports provided at the inlet and outlet of the reactor.

Legend

1. Butane cylinder
2. Air compressor
3. Surge tank
4. Moisture trap
5. CO₂ trap
6. Capillary flowmeter
7. Mixing chamber
- 8a,8b. Sampling ports
9. Preheater
10. Electric coil
11. Catalyst bed
12. Condenser
- V₁, V₂. Needle valves
- TC₁, TC₂. Thermocouples

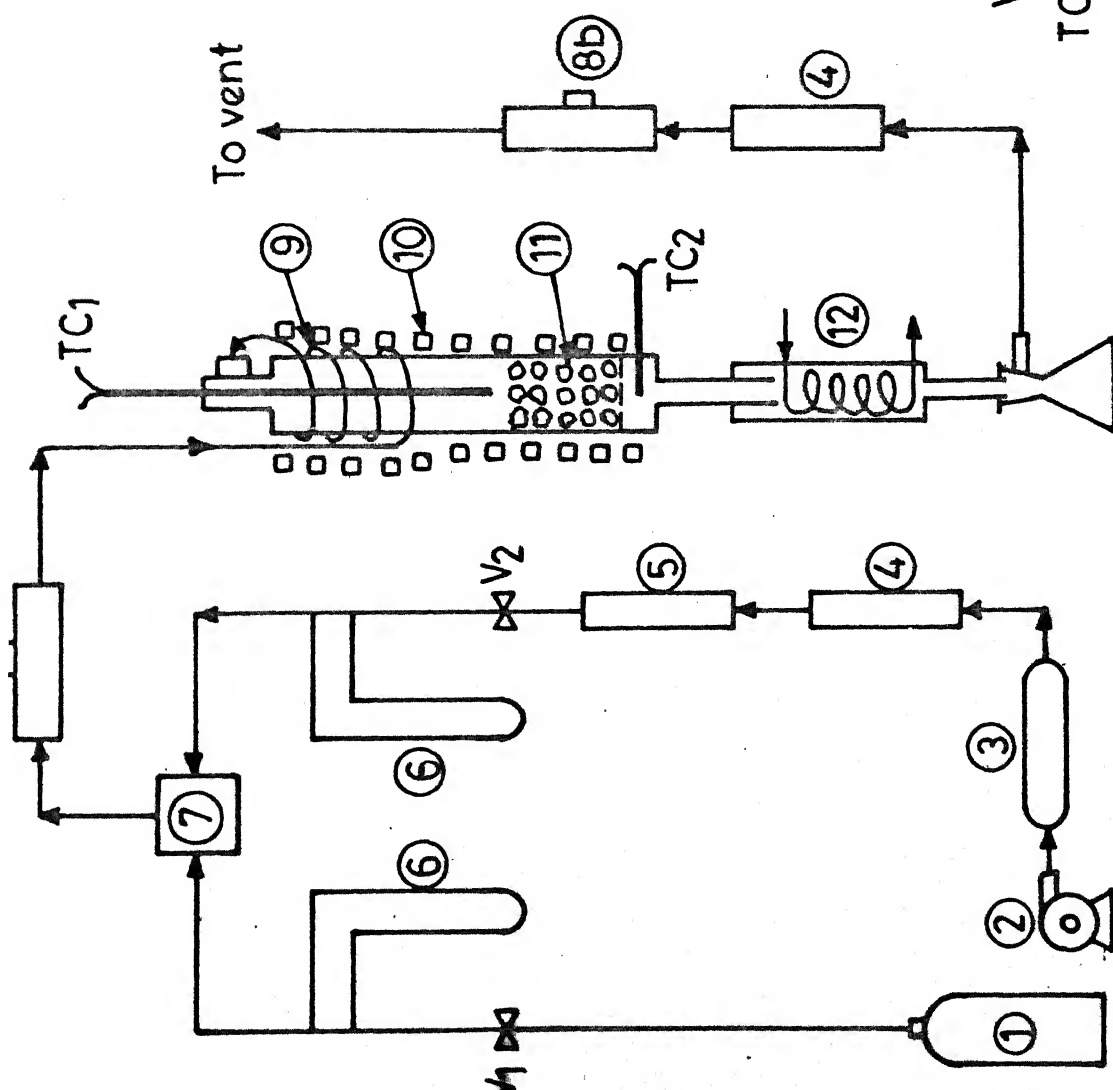


Fig.3.1 - Experimental setup.

3.4 Experimental Procedure:

The reactor was packed with a given amount of the catalyst. Air supply was switched on, adjusted to the required flow-rate by needle valve V_2 and the catalyst bed temperature was raised gradually to the desired level. When the catalyst bed temperature was steady, n-butane was introduced and adjusted to the predetermined flow rate with a needle valve V_1 . The compositions of the feed as well as the exit gaseous streams were determined by chromatographic analysis.

At the end of the experiment n-butane supply to the reactor was shut off. However, the air supply was maintained for some time to ensure elimination of coke deposition and to gradually cool the reactor contents.

3.5 Analytical Methods:

The gaseous products were analysed by an HP-5890A gas chromatograph equipped with a single filament thermal conductivity detector and a 3390 A digital integrator. A 2000 mm Durapack column of 3 mm O.D. was used to resolve carbon dioxide and n-butane at 30°C. A 1200 mm molecular sieve 5A column of 3 mm O.D. was used to resolve carbon monoxide, oxygen and nitrogen at 30°C. The following operating conditions were used.

Carrier gas : H₂
Injector temp. : 100°C
Detector temp. : 200°C
Oven temp. : 30°C
Column flow : 20 \pm 1 ml/min
Reference flow : 30 \pm 1 ml/min

Sample chromatograms are shown in Figures 3.2 and 3.3.

Pure samples obtained from Matheson Gas Company were used for calibrations. The gas samples were injected using a 0.5 ml gas-tight Hamilton syringe. The retention times and the calculated response factors are presented in Table 3.2.

The composition of a component is obtained by

$$\text{Composition} = \frac{\text{Integrator response} \times \text{Response factor}}{\text{Injected volume}}$$

The maleic anhydride content was computed by carbon balance.

A sample calculation is given in Appendix-1.

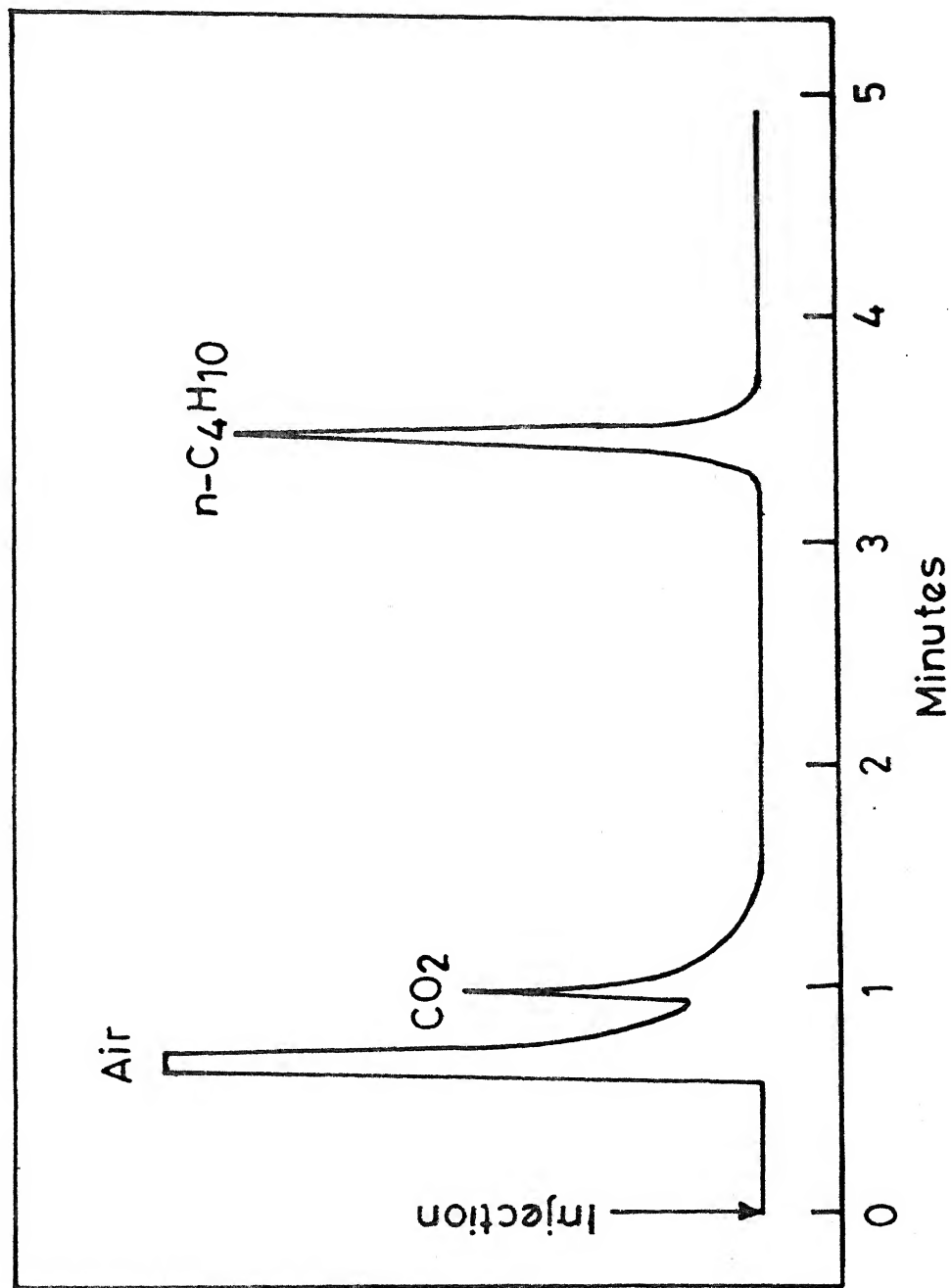


Fig.3.2 - Resolution of CO₂ and n-C₄H₁₀ on Durapak column at 30°C.

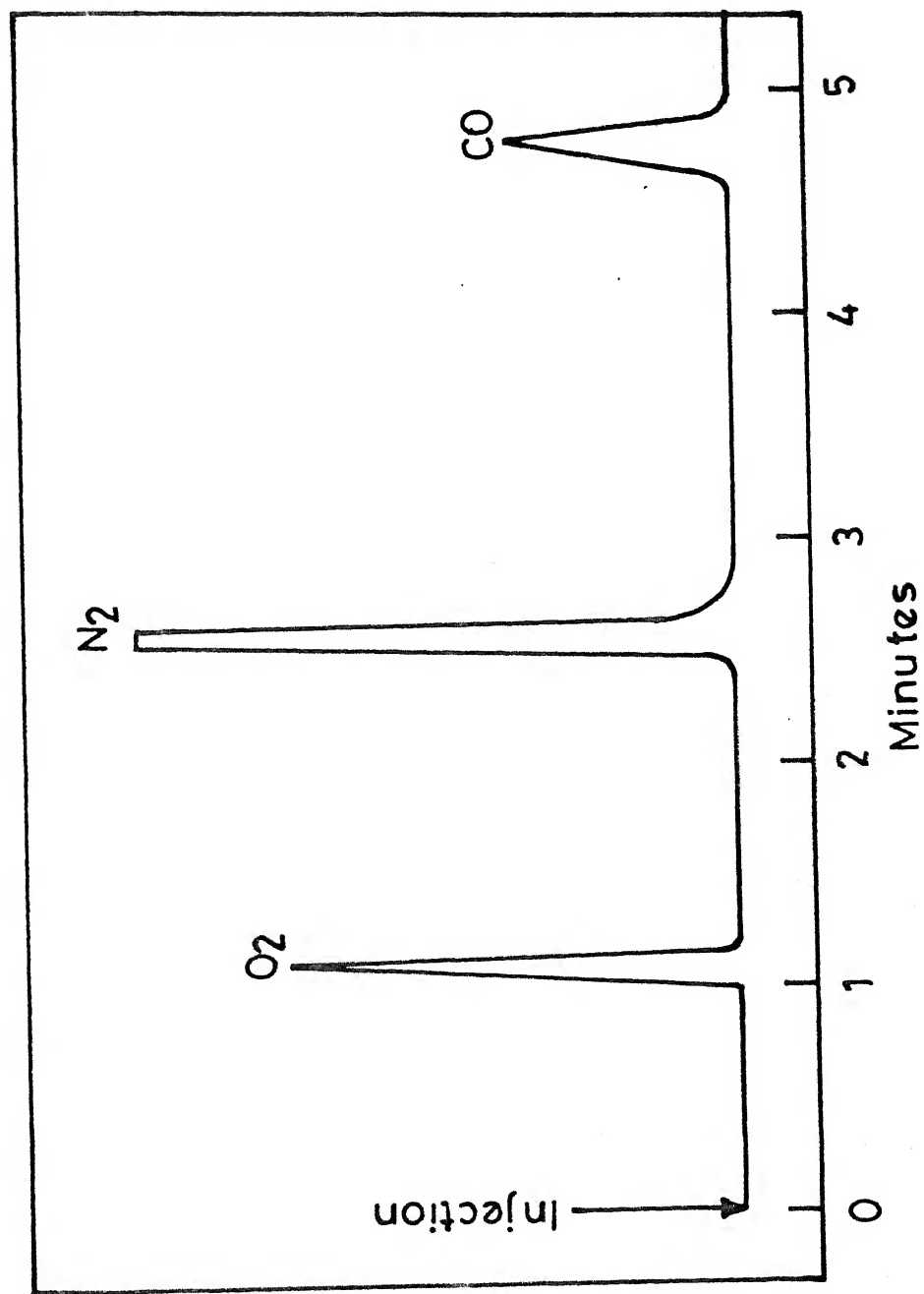


Fig. 3.3 - Resolution of O₂, N₂, CO on molecular sieve 5A column at 30°C.

TABLE 3.2: RETENTION TIMES AND RESPONSE FACTORS

Column	Component	Retention time, min	Response factor $\times 10^{13}$ mol/integrator response
Durapak	CO ₂	1.00	0.8362
	n-butane	3.46	1.5694
Molecular sieve 5A	O ₂	1.10	0.8093
	N ₂	2.56	0.8043
	CO	4.76	0.7864

CHAPTER 4

CHARACTERIZATION OF CATALYSTS

Solid state properties like crystal structure, thermal stability and surface area influence the catalytic behaviour of solids. Determination of these properties, therefore, is necessary to understand the catalytic nature of the solids and to elucidate the reaction mechanism. The catalysts used in the present study were characterised in terms of crystal structure by means of X-ray diffraction (XRD), thermal stability by means of differential thermal analysis (DTA) and thermogravimetric analysis (TGA), and surface area by the BET method.

4.1 X-Ray Diffraction Studies:

The X-ray diffraction technique was used to determine the phases present in the catalysts. The powdered samples were examined with a Seifert Iso-debyeflex 2002 X-ray generator using a Seifert M2III goniometer and diffractometer under the following experimental conditions.

The samples were scanned between 10° and 80° (2θ)

Radiation	: $\text{CuK}\alpha$ with Ni filter
Width of receiving slit	: 0.3 mm
Width of scanning slit	: 2.0 mm
Scanning speed	: 1.2° (2θ)/min
Chart speed	: 3 cm/min
Count rate	: 500/s
Time constant	: 10 s

The d-spacings for the reflections were calculated using the Bragg's equation.

$$2 \times d \sin\theta = n \lambda$$

The measured 'd' values for catalysts A and B are shown in Table 4.1. Both the catalysts show two identical weak reflections at $12.4^\circ (2\theta)$ and $29.6^\circ (2\theta)$.

The XRD patterns for both the catalysts are shown in Fig.4.1. Both the catalysts were found to be poorly crystalline which is typical of VPO catalysts calcined at low temperatures. Since the catalysts show only two reflections, identifications of the phases present was not possible. However, as the reflections for both the catalysts A and B were identical, it can be inferred that the small amount of iron present in catalyst B does not bring about a crystalline modification. It is probable that the iron is incorporated in the vanadium phosphate complex crystallites without affecting the crystalline structure.

4.2 Thermal Studies:

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) on both catalysts A and B were carried out in order to obtain information regarding transitions, energies involved during the transformations and weight losses accompanying the transformations.

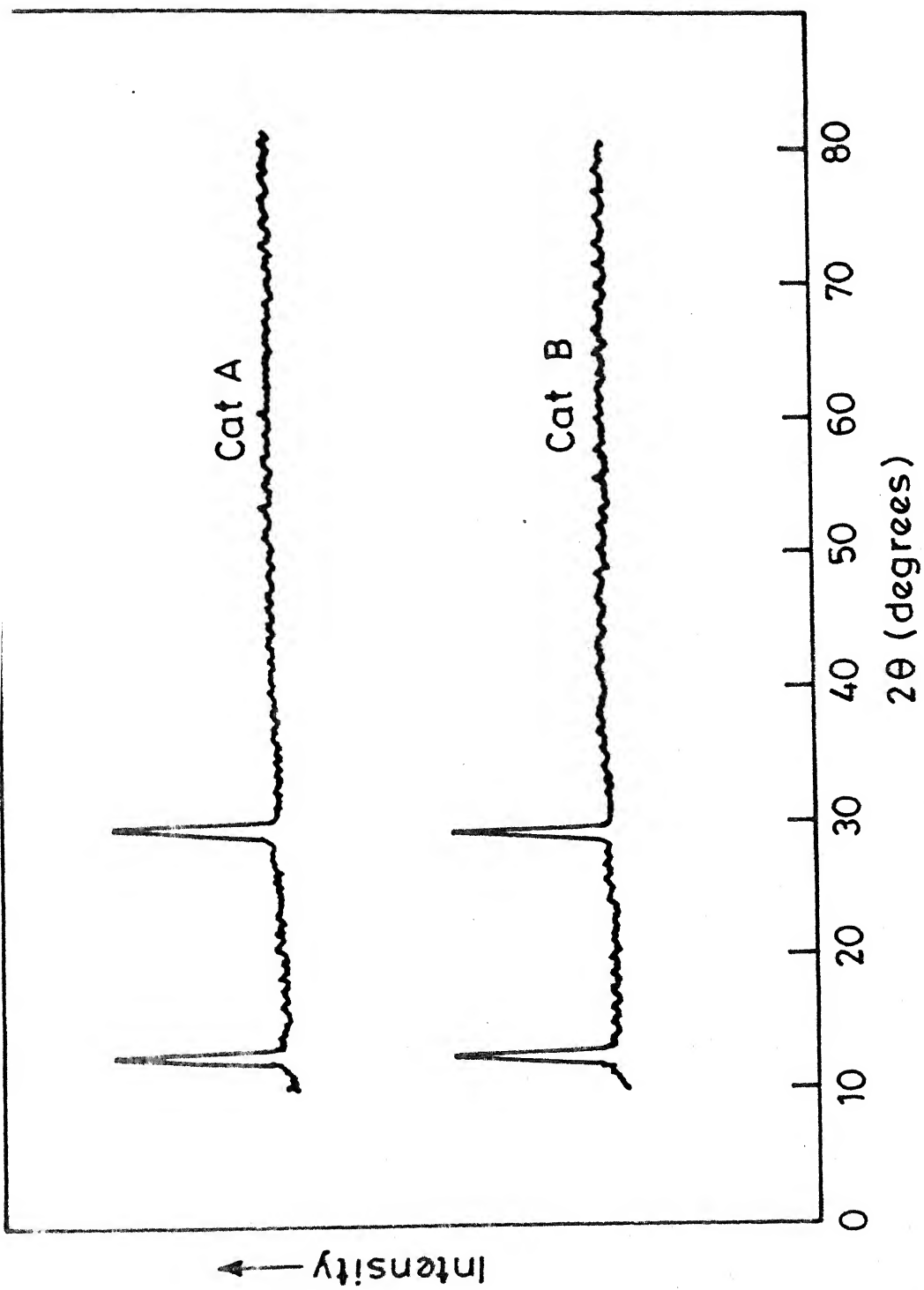


Fig.4.1 - XRD patterns of catalysts A and B.

TABLE 4.1: 'd' VALUES FOR CATALYSTS A AND B

Catalyst	$d(\text{\AA})$	I/I_0
A	7.130	100
	3.014	100
B	7.130	100
	3.014	100

The DTA and TGA curves for the catalysts samples were recorded using M.O.M. Derivatograph with platinum -platinum rhodium thermocouple, as the temperature sensing element. The samples were heated in an alumina crucible at a rate of 10°C/min using α -alumina as the reference material.

The DTA thermograms for catalysts A and B are shown in Fig.4.2. The DTA curve for catalyst A does not show any peaks indicating no phase transitions. However, if any phase transitions are present they do not involve significant energies of absorption or release. In the case of catalyst B the DTA curve shows an endotherm at 525°C. Since iron was introduced as ferric nitrate in catalyst B, it is possible that free ferric nitrate in the catalyst sample decomposes at this temperature leaving iron oxide.

The TGA curves for catalysts A and B are shown in Fig. 4.3. Both these thermograms do not show any weight losses during the heating process indicating that there were no phase transitions involving weight changes.

4.3 Surface Area:

The surface area measurements for the catalysts were carried out using the single point BET apparatus with quonto-chrome, model OS-7 using liquid nitrogen as adsorbent. The results are presented in Table 4.2.

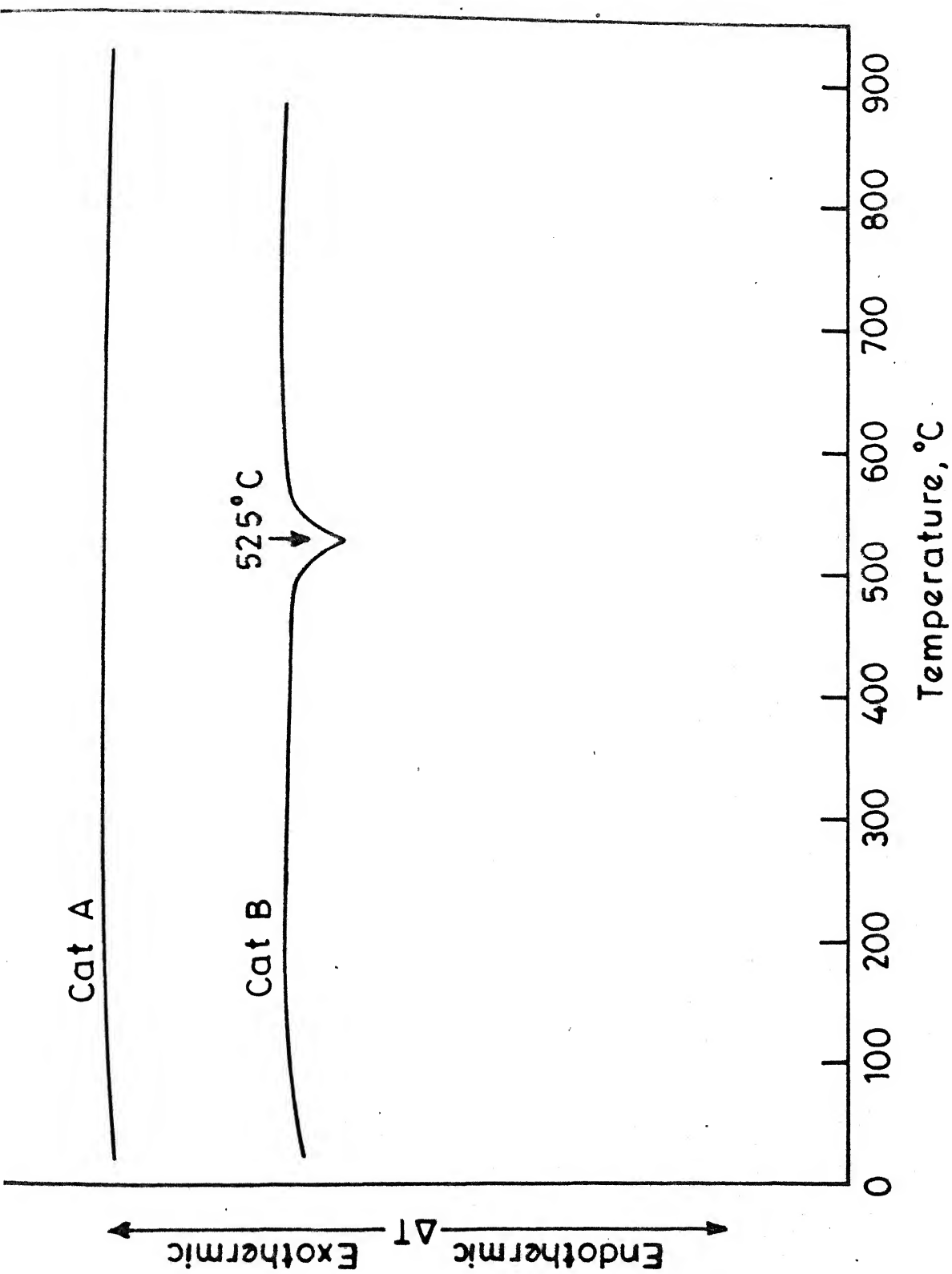


Fig.4.2 - DTA curves of catalysts A and B.

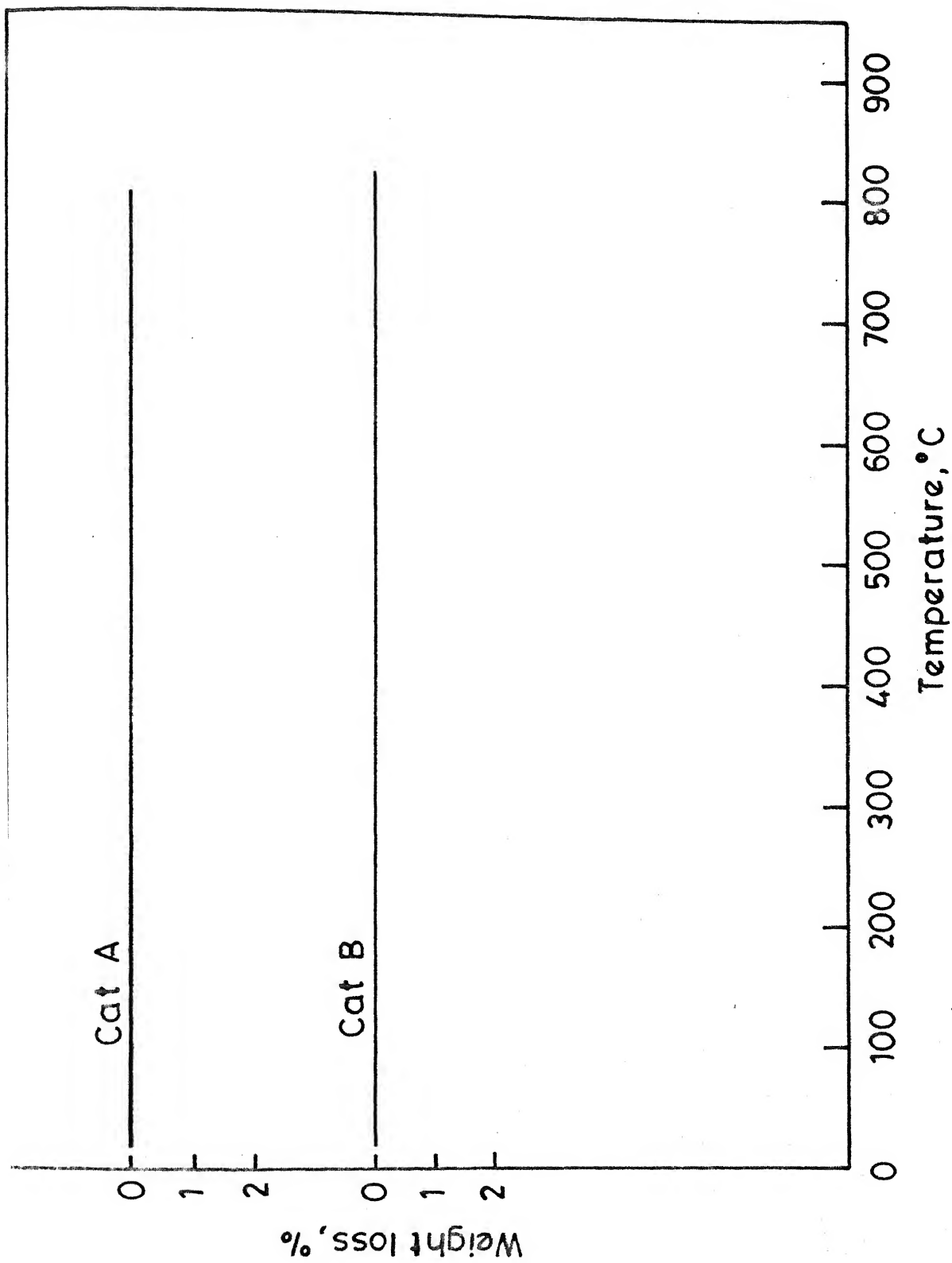


Fig.4.3 - TGA curves of catalysts A and B.

TABLE 4.2: SURFACE AREAS OF CATALYSTS A AND B

Catalyst	Specific surface area m^2/g
A	58
B	61

Thus both the catalysts have nearly the same surface area. The presence of iron in catalyst B did not result in a major surface area modification.

CHAPTER - 5

RESULTS AND DISCUSSION

The products of n-butane oxidation on both catalysts A and B included maleic anhydride and carbon oxides. Products such as butenes, butadiene, furan etc. were found to be absent.

5.1 Reproducibility of the Experimental Results:

Preliminary experiments indicated that steady-state was attained after the catalyst was exposed to the reaction medium under the experimental conditions for nearly six hours. Hence, all the experimental data were recorded six hours after a run was started. The data are given in Appendix 2 in the form of tables for Run Nos: 1 - 92. One run was repeated five times under nearly identical conditions to verify reproducibility. The product distribution for replicate runs is presented in Table 5.1. The conversion, yield and selectivity of these replications are presented in Table 5.2. It is noted that the results are fairly reproducible with the following standard deviations for the conversion, yield and selectivity respectively.

$$s_{\text{conv}} = 0.74$$

$$s_{\text{yield}} = 0.34$$

$$s_{\text{selectivity}} = 0.25$$

TABLE 5.1 DATA ON PRODUCT DISTRIBUTION FOR REPLICATE
RUNS (ON DRY BASIS)

Catalyst : B
W/F : 6 g/(mg mol/s)
n-butane conc. in air : 1.0 mol/100 mol mixture of
air and n-butane
Temperature : 375°C

Products (mole%)	Replication No.				
	1	2	3	4	5
Butane	0.560	0.545	0.550	0.549	0.561
MA	0.214	0.220	0.216	0.219	0.21
CO ₂	0.598	0.602	0.607	0.610	0.59
CO	0.308	0.310	0.311	0.313	0.30

TABLE 5.2 RESULTS OF REPLICATE RUNS

Replication no Results *	1	2	3	4	5
Conversion* of n-butane, mol%	44.0	45.5	45.0.	45.1	43.8
Yield** of MA mol%	21.4	22.0	21.6	21.9	21.2
Selectivity*** towards MA, mol%	48.6	48.4	48.0	48.6	48.4

$$* \text{ conversion, \%} = \frac{\text{mol butane converted}}{\text{mol butane fed}} \times 100$$

$$** \text{ yield, \%} = \frac{\text{mol MA formed}}{\text{mol butane fed}} \times 100$$

$$*** \text{ selectivity, \%} = \frac{\text{mol MA formed}}{\text{mol butane converted}} \times 100$$

Model calculations for these quantities are given in
Appendix - 1.

5.2 Mass Transfer Aspects:

In reactions catalysed by solids the mechanism involves diffusion of chemical species in the bulk fluid phase (external mass transfer) and in the pores of the catalyst (intraparticle mass transfer) besides the chemical reaction, adsorption and desorption on the surface of the catalyst. If the rates of external mass transfer and intraparticle mass transfer are kept high in comparison to the rate of chemical reaction, the complex mechanism is reflected only by the surface reactions and hence leads to an understanding of reaction kinetics.

Limitations of external mass transfer resistance can be eliminated by a proper choice of linear velocity of the reactants through the reactor. This can be achieved by conducting experiments at different flow rates of the reacting fluid keeping contact time (represented by W/F) constant. Fig. 5.1 shows the effect of flow rate on conversion, yield and selectivity at constant space velocity. It can be seen that the responses are insensitive to flow rates beyond a value of about 1000 ml/min. Thus, all the experimental runs were carried out at flow rates in excess of 1000 ml/min, when the influence of external mass transfer was completely eliminated.

In a few experiments the particle size of one of the catalysts was changed using identical experimental conditions.

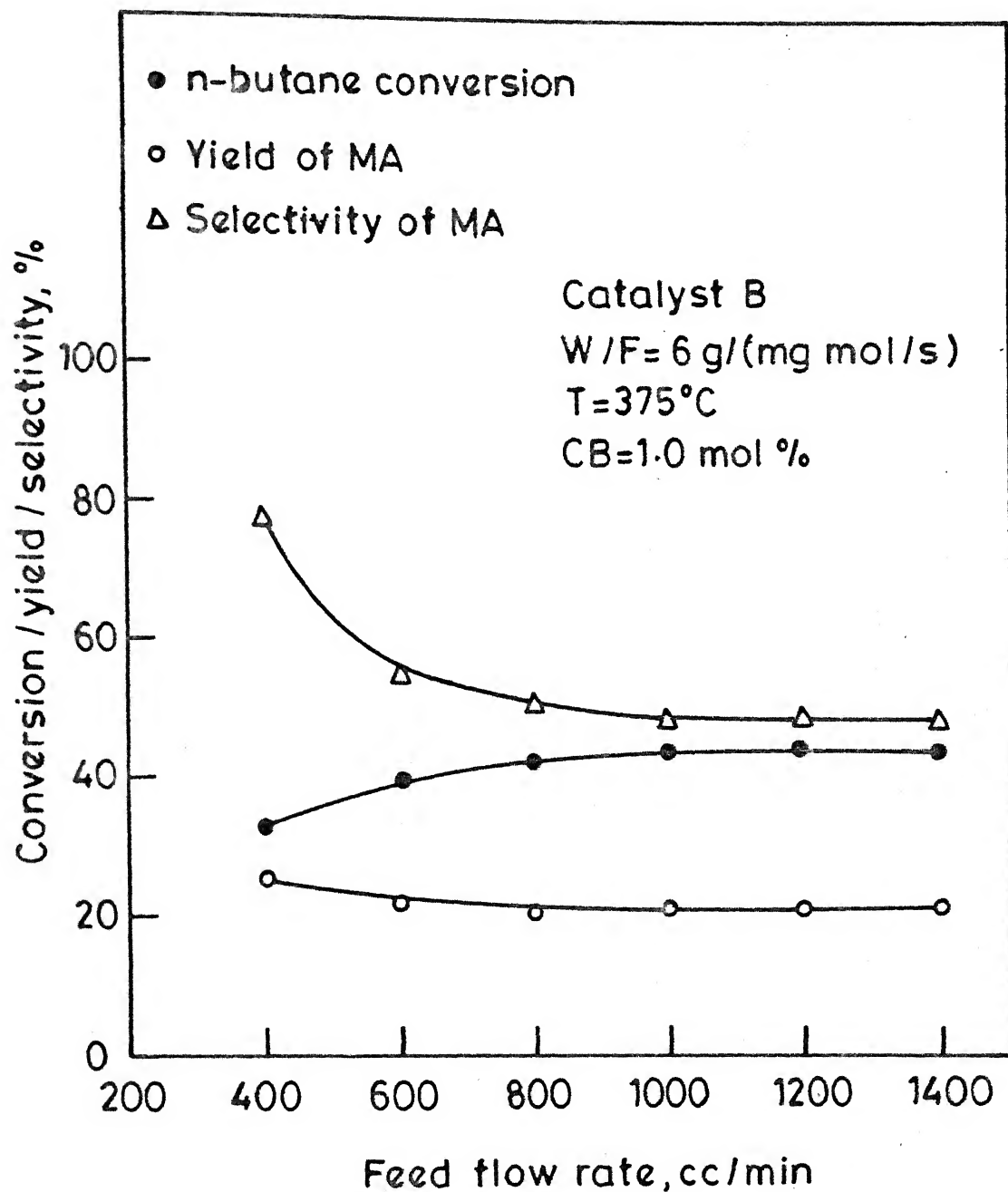


Fig. 5.1 - Effect of flow rate on responses at constant space velocity.

The results are shown in Table 5.3. It is seen that no significant changes occurred either in the conversion or yield of malic anhydride indicating thereby absence of intraparticle resistance.

5.3 Heat Transfer Aspects:

Although the oxidation reaction is exothermic, the use of low levels of butane concentrations in the feed stream (0.6 -1.2 mol% in air) allowed the reactor to be operated at near isothermal conditions. The maximum observed temperature difference between the inlet and outlet was found to be only 2°C.

5.4 Effect of Contact Time on Conversion, Yield and Selectivity:

The contact time of the reactants with the catalyst bed is represented by the ratio of catalyst bed weight (w) to flow rate of the reactants (F). An increase in W/F value represents an increase in contact time. To study the effect of contact time on the responses, experiments were conducted at five values of W/F ranging from 3 to 9. These W/F values correspond to contact times ranging from 0.16 s to 0.48 s. Fig. 5.2 shows the effect of W/F on n-butane conversion for catalyst A as well as for catalyst B. The conversion is found to increase in both cases reflecting the irreversible nature of the reaction. It is also noted from these plots that catalyst A is much more active than catalyst B despite the fact that the surface area of both the catalysts is

TABLE 5.3 EFFECT OF PARTICLE SIZE OF CATALYSTS ON RESPONSES

Catalyst : B
 W/F : 6 g/(mg mol/s)
 Temperature : 375°C
 n-butane conc : 1.0 mol%
 in feed

Responses	Particle size	
	- 18 + 25	- 80 + 100
Conversion, %	44.0	45.10
Yield, %	21.40	21.23
Selectivity, %	48.64	47.07

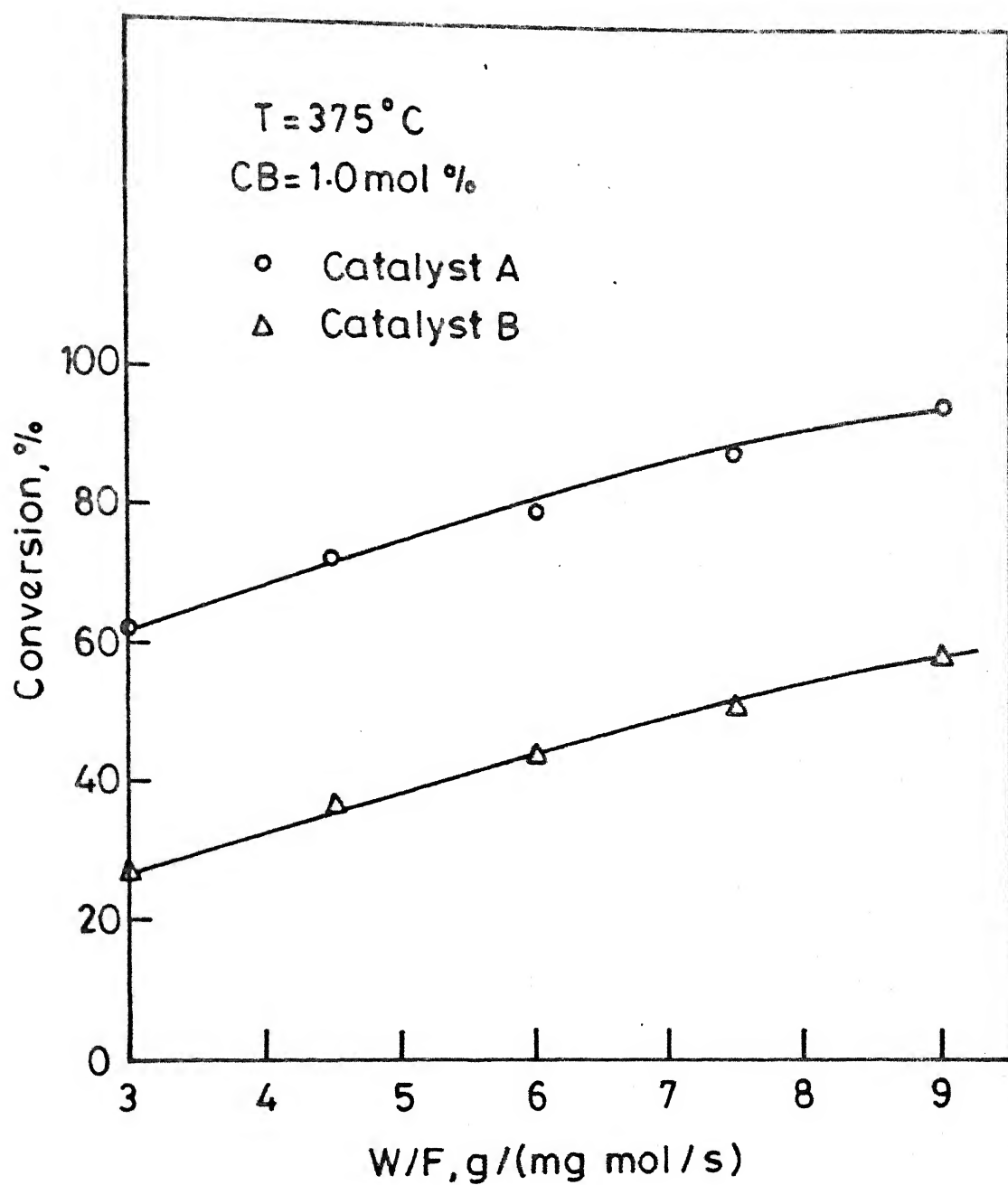


Fig.5.2 - Effect of contact time on conversion.

almost the same. It is possible that the small amount of Iron present in catalyst B increases the bond strength between surface oxygen ions and the surface and thus decreases the reducibility of the catalyst. It has been established that oxidation reactions on vanadium oxide-based catalysts follow the redox mechanism first proposed by Mars and Van Krevelen. Hence, a decrease in the reducibility of the catalyst results in a decrease in its activity.

Fig. 5.3 shows the effect of W/F on the yield of maleic anhydride for catalyst A as well as for catalyst B. The conversion and yield in both the cases are found to increase with increase in contact time. It is noted that catalyst B gives better yield of maleic anhydride than catalyst A. Since the activities of catalysts A and B are different the steady-state surface compositions (vanadium to oxygen ratio) of the catalysts would be different. The iron present in catalyst B is probably responsible for attaining a surface composition having higher selectivity towards maleic anhydride. Fig. 5.4 shows the selectivity curves for catalyst A as well as catalyst B. The selectivity increases for both catalysts A and B. However, catalyst B is found to be more selective than catalyst A.

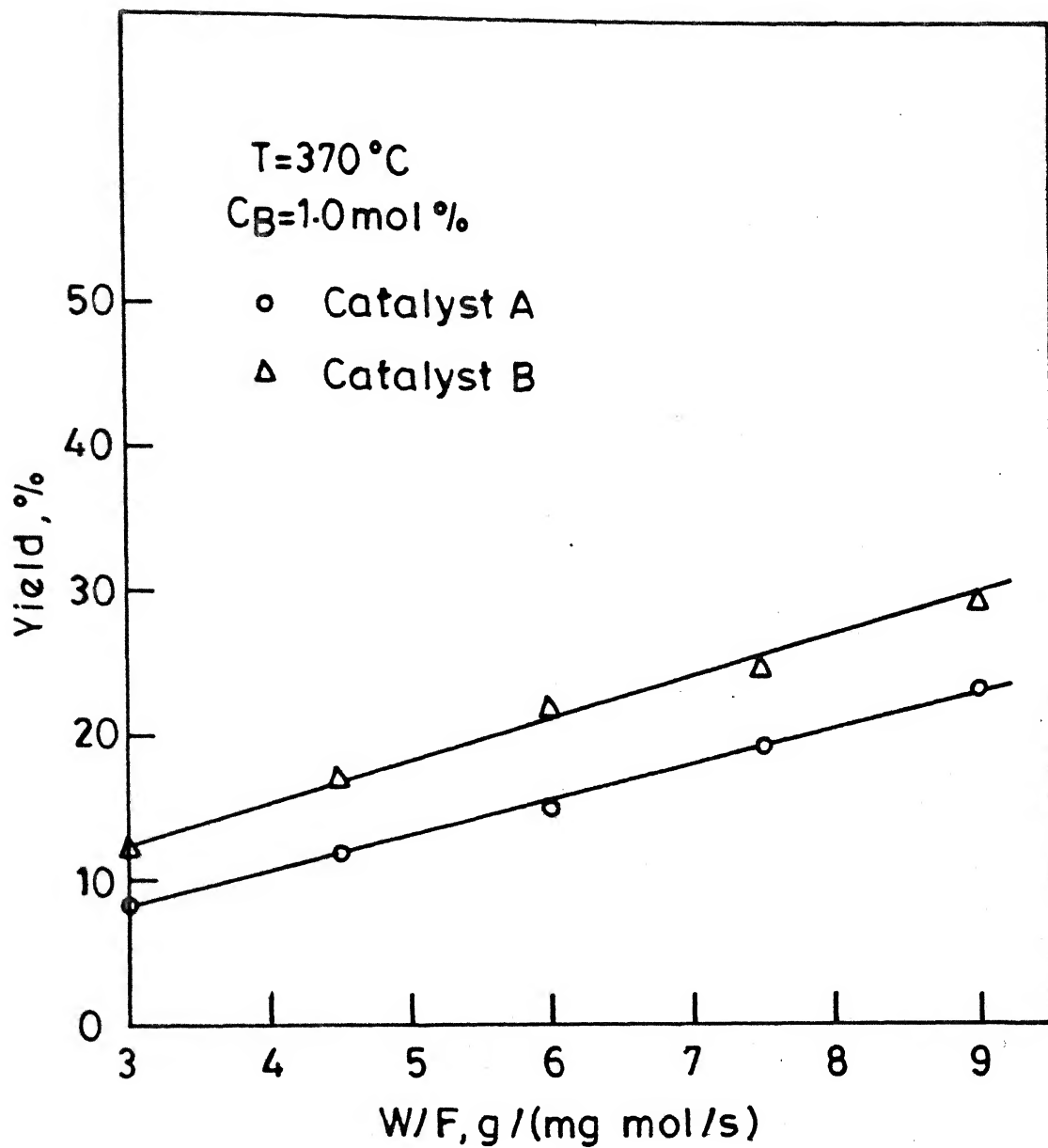


Fig.5.3 - Effect of contact time on yield.

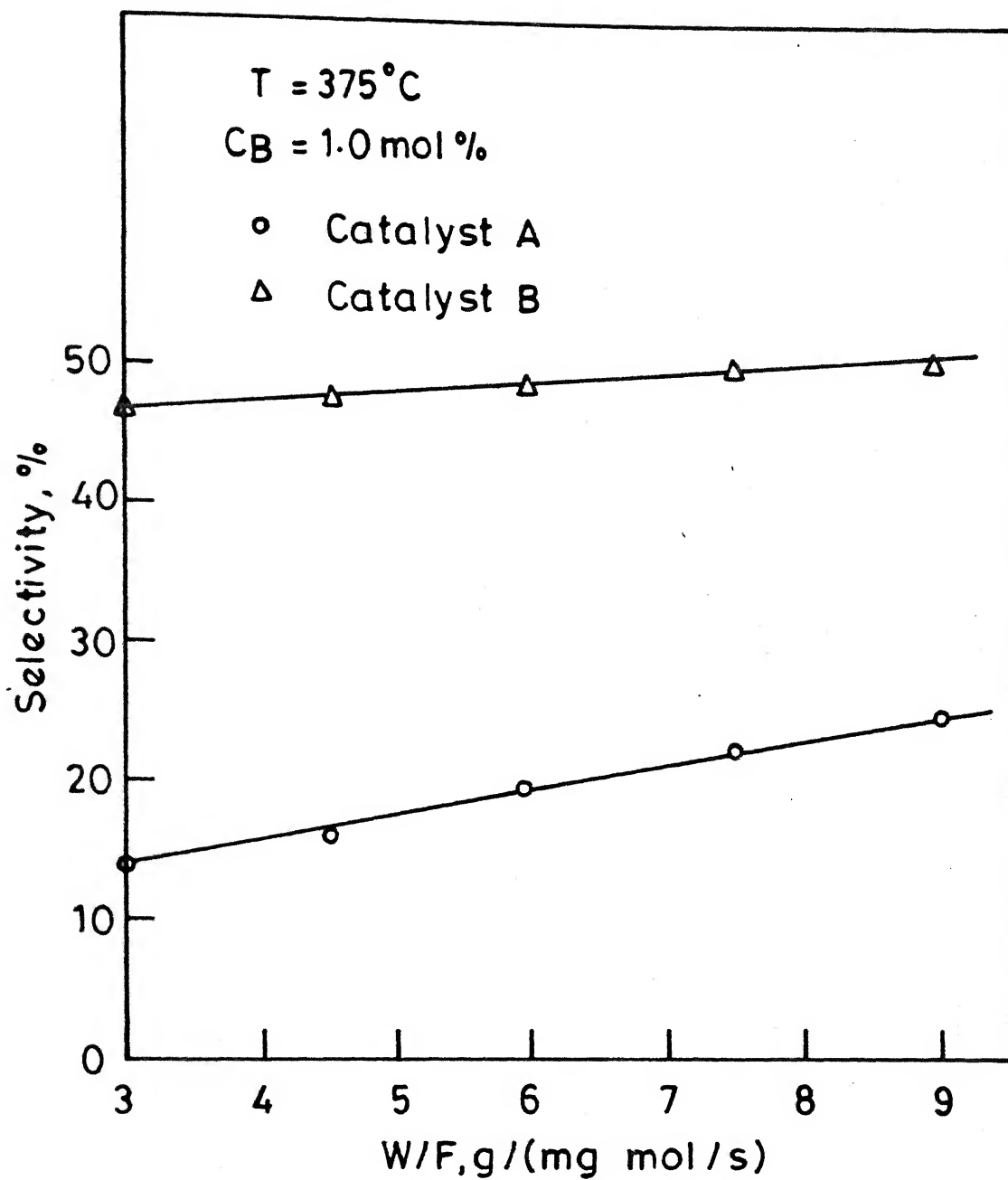


Fig.5-4 - Effect of contact time on selectivity.

5.5 Effect of n-butane Concentration in Feed on Conversion, yield and Selectivity:

Since the reactor feed comprised of low concentrations of n-butane in air, Oxygen was in much excess of n-butane. For this reason, the concentration of oxygen remained nearly constant in all the experiments. Hence, a variation in the n-butane content of the feed would show effect on the responses. Accordingly experiments were conducted at four levels of n-butane concentrations in the feed. Fig. 5.5 shows the effect of n-butane concentration on conversion using catalysts A and B. The conversion is found to increase linearly with an increase in the reactant concentration in both the cases. However, the increase in the case of catalyst A is much more pronounced. The steady-state surface composition of the catalyst is also dependent on the bulk fluid hydrocarbon concentration as lattice oxygen is drawn up by the hydrocarbon molecule during oxidation. Hence, an increase in hydrocarbon concentration results in a more reduced state of the catalyst. Fig. 5.6 shows the effect of n-butane concentration on yield for both the catalysts. For both catalysts, the yield is found to decrease with increase in n-butane concentration. A maximum occurs between 1.5 and 1.7 mole% for catalyst A. Fig 5.7 shows the effect of n-butane concentration on selectivity for both the catalysts. The selectivity is found to decrease with an increase in n-butane concentration in both the cases.

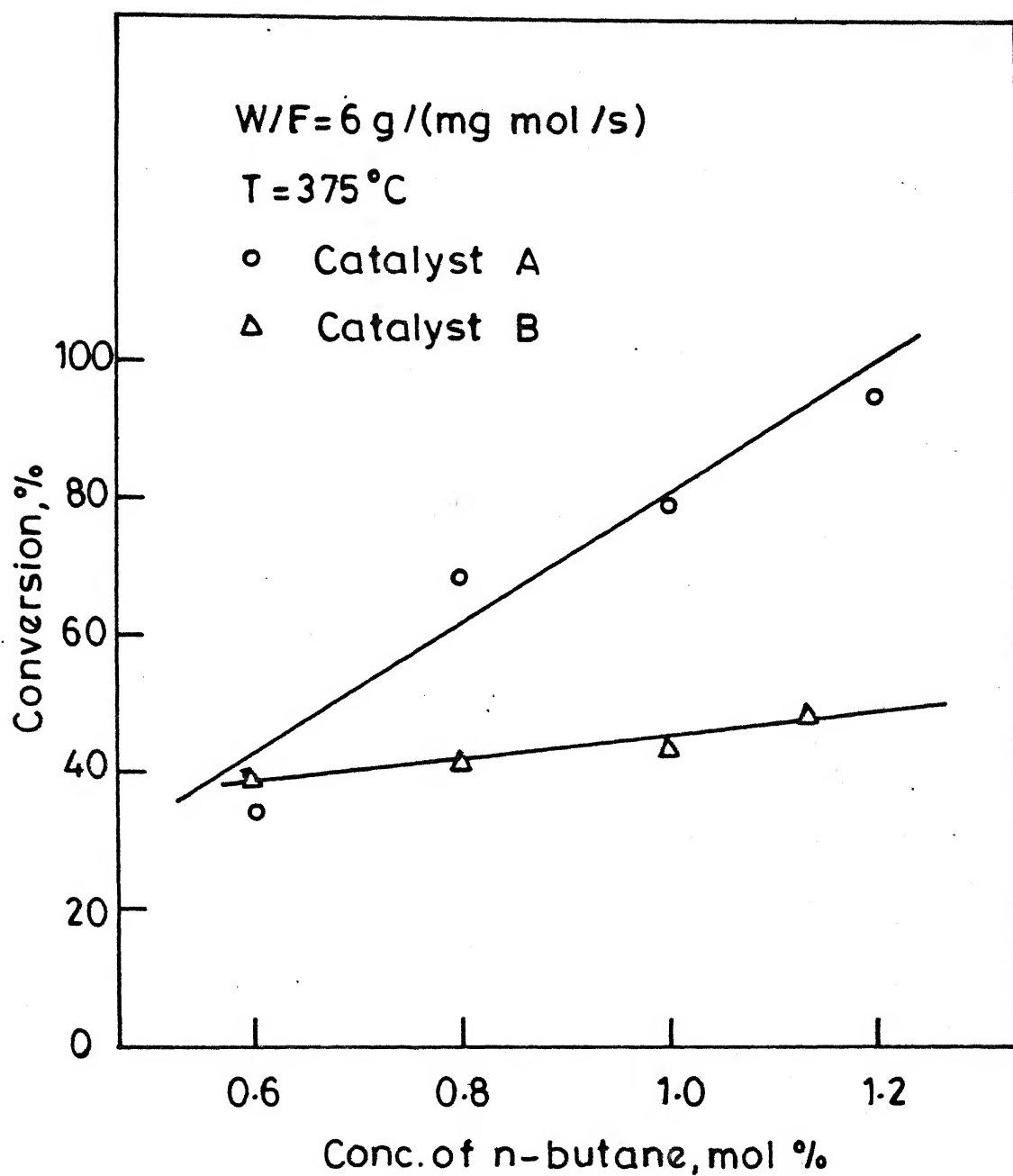


Fig. 5.5 - Effect of n-butane concentration on conversion.

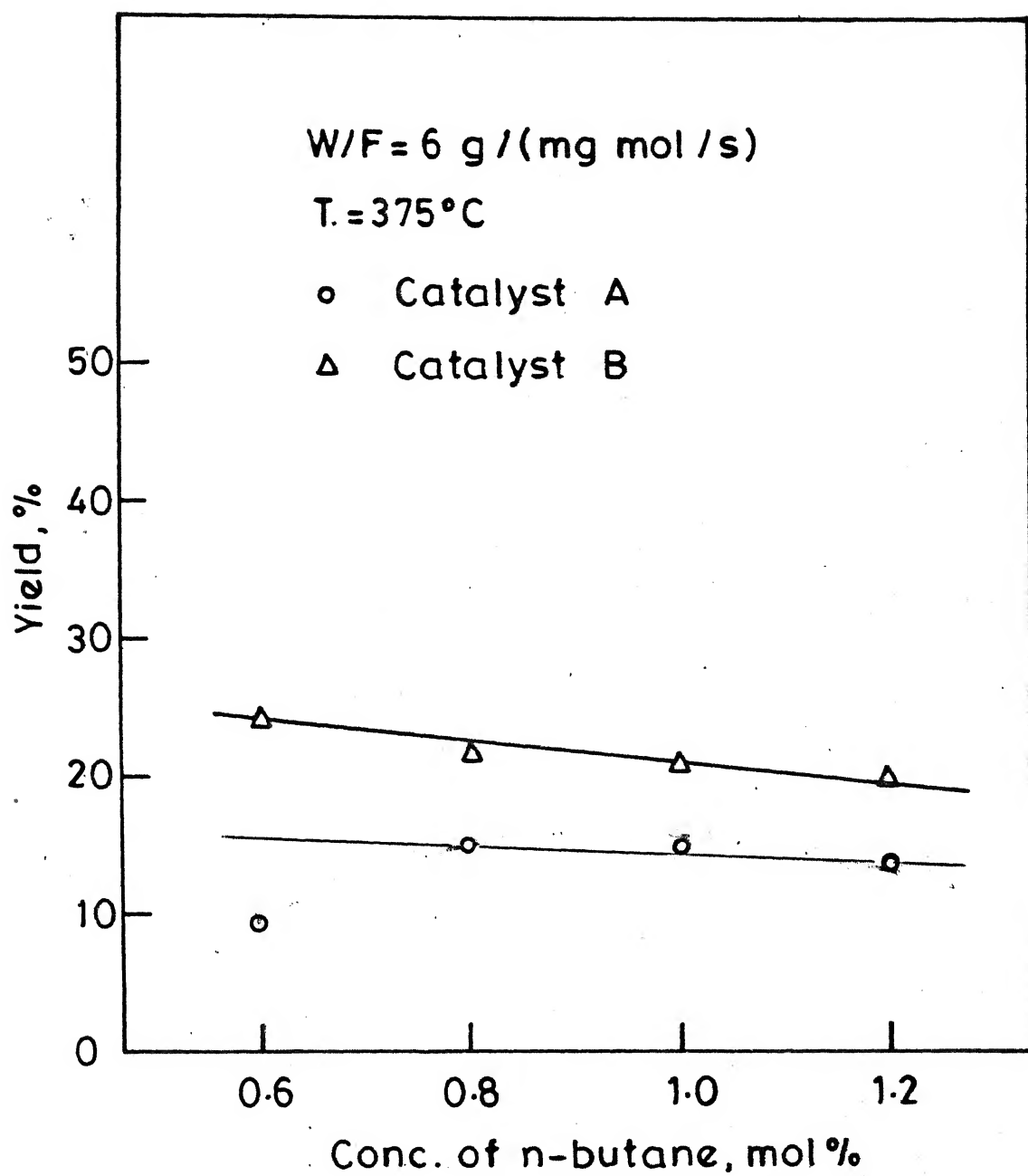


Fig.5.6 - Effect of n-butane concentration on yield.

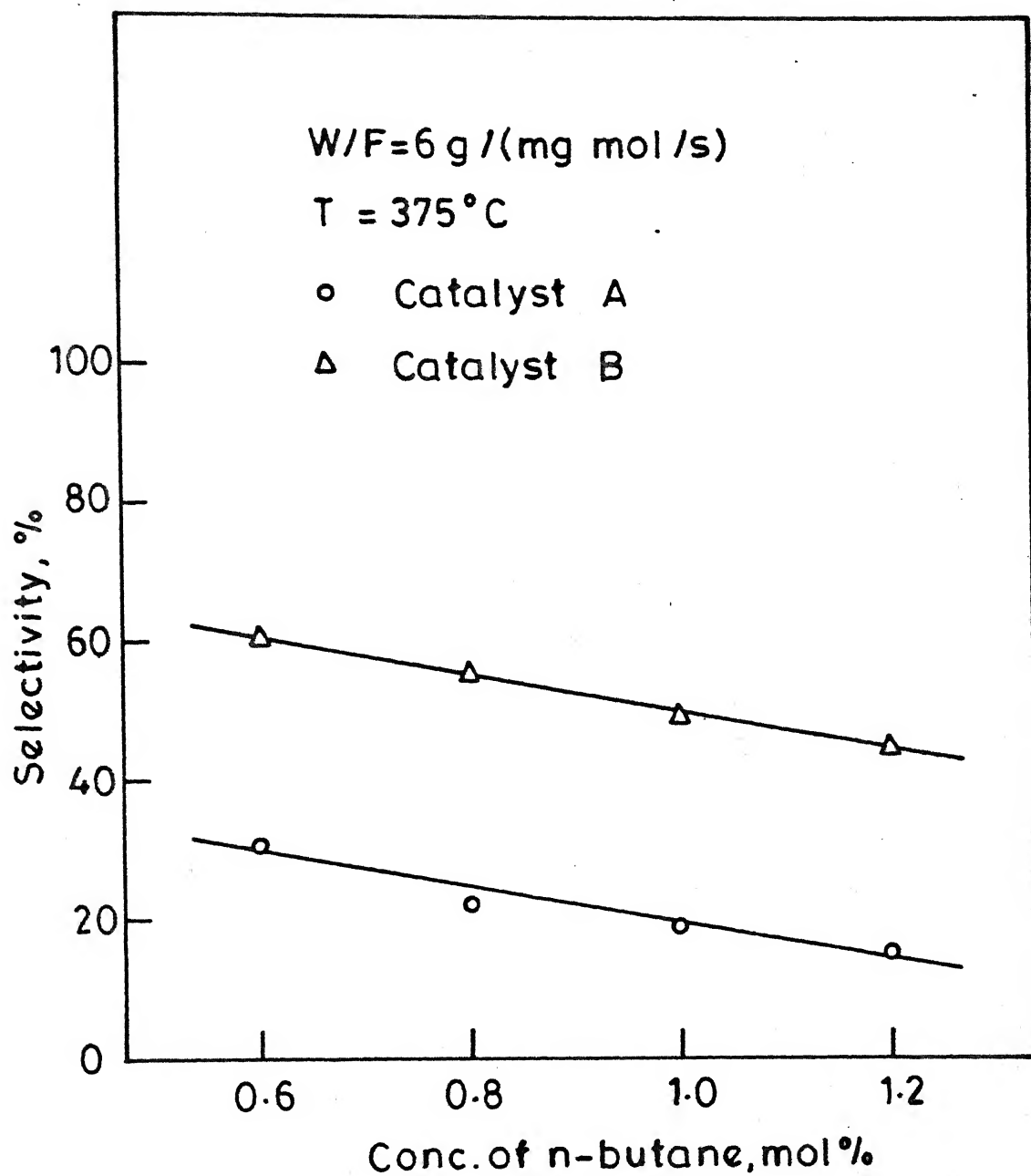


Fig.5.7 - Effect of n-butane concentration on selectivity.

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5.6 Effect of Temperature on Conversion, Yield and Selectivity:

In a complex reaction, different individual reactions may be influenced to different extents by temperature variations depending on the activation energies involved. Consequently, a wide range of product distributions may be obtained at different temperatures. A study of the effect of temperature on conversion, yield and selectivity would give information on the location of optimum operating temperature to obtain a favourable product distribution. Hence, experiments were conducted at five temperatures in the range of 300°C to 400°C. Fig 5.8 shows the effect of temperature on conversion of n-butane for catalysts A and B. An increase in conversion with temperature is noted in both the cases. Fig 5.9 shows the effect of temperature on selectivity. The selectivity is found to decrease with increasing temperature. However, drop in selectivity in the case of catalyst A is gradual over the temperature range studied whereas in the case of catalyst B it is rather steep after 350°C.

The effect of temperature on yield for catalyst A and B is shown in Fig 5.10. Maximum yield is found to occur at a temperature of around 375°C. It is probable that at higher temperatures decomposition of maleic anhydride becomes significant.

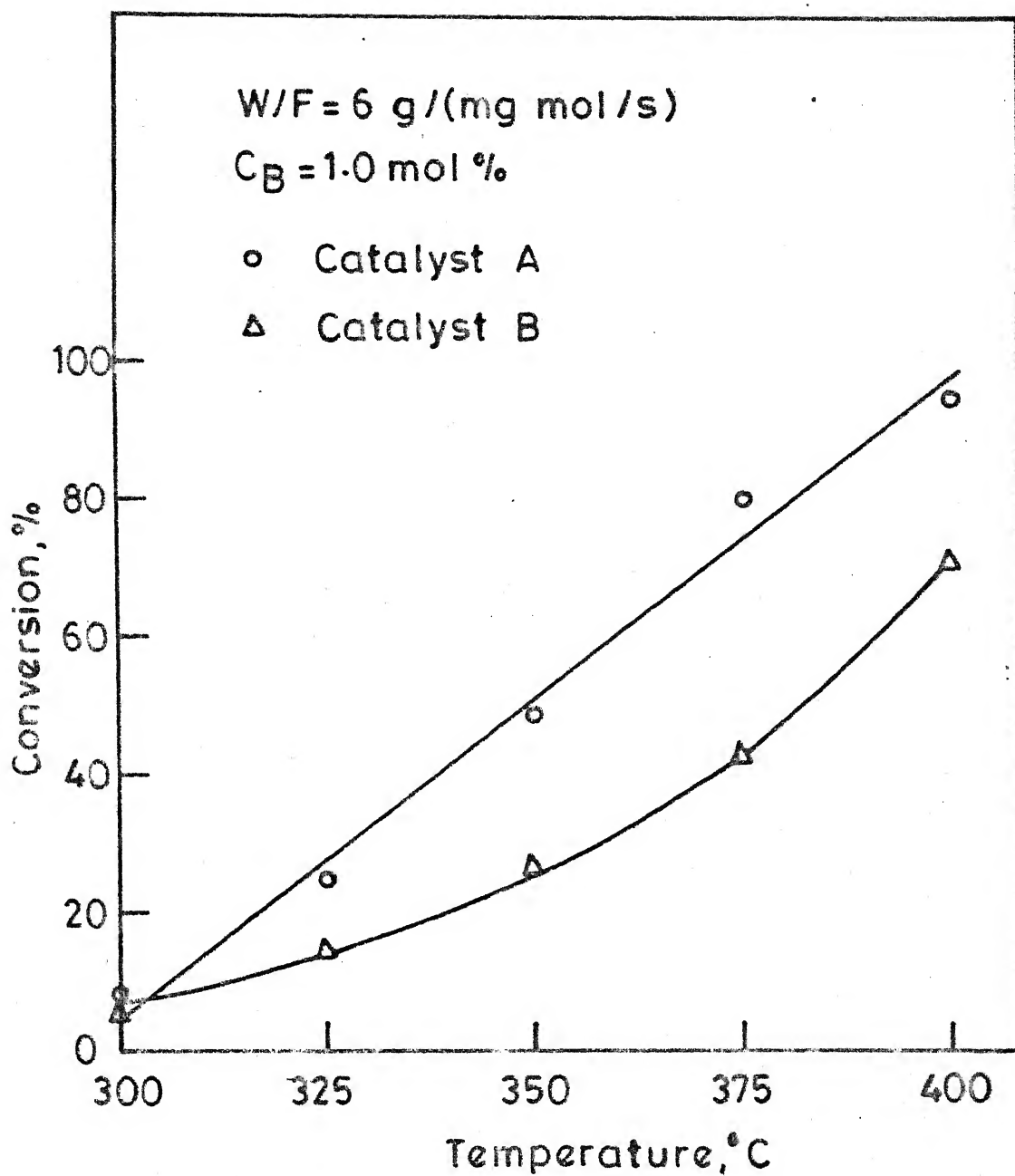


Fig. 5.8 - Effect of temperature on conversion.

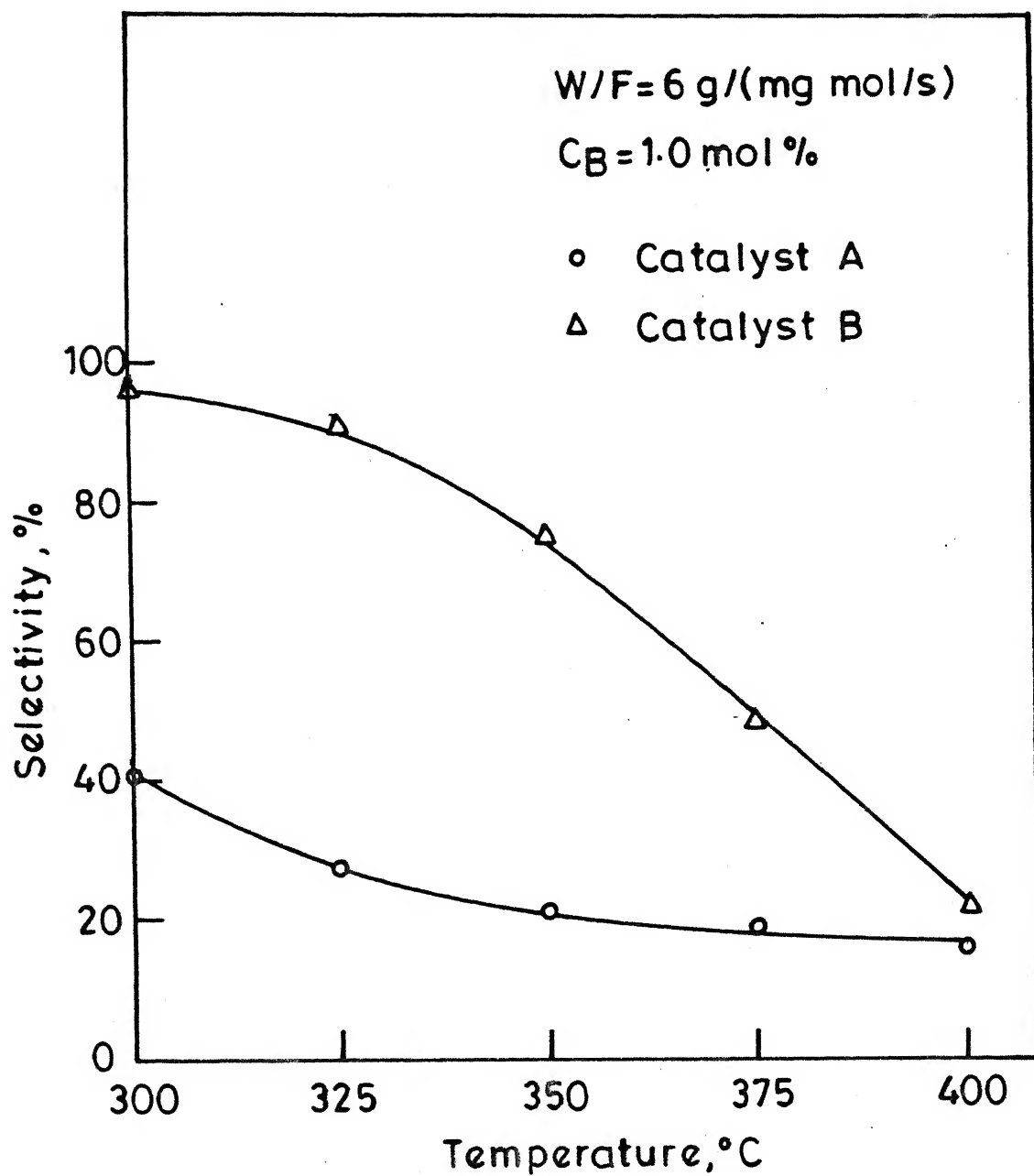


Fig.5.9 - Effect of temperature on selectivity.

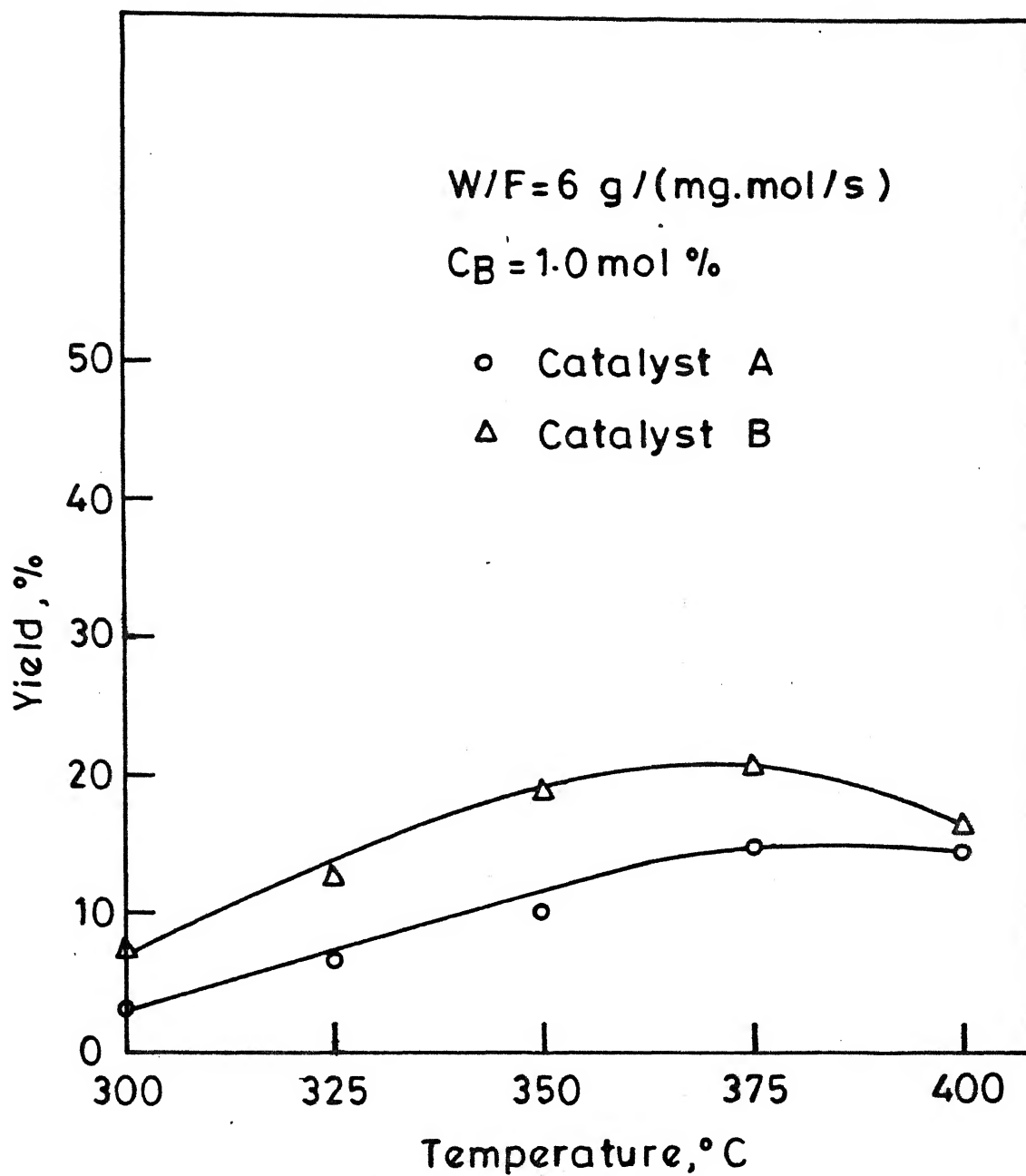


Fig.5.10 - Effect of temperature on yield.

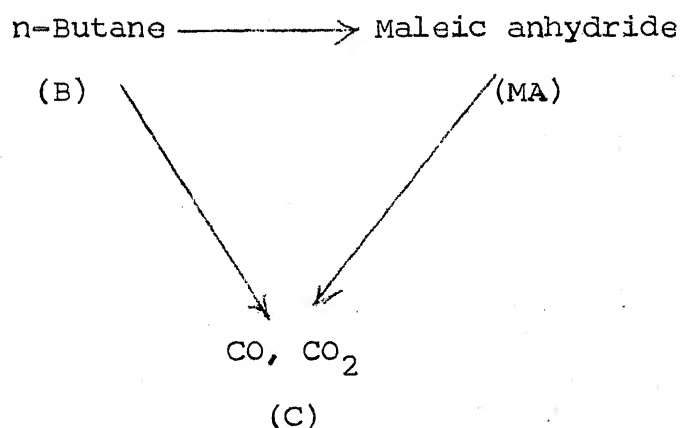
CHAPTER - 6KINETIC MODELLING

A kinetic model describing the catalytic reaction leads to a better understanding of catalysis. Further, an accurate model allows reasonable extrapolation outside the ranges of the variables concerned. The reactor behaviour can then be predicted at various values of variables, which eventually provide the basis for optimizing a given situation. Though the form of the model equation is not known a priori, the range of the forms of model equations in heterogeneous catalysis are limited by physico-chemical laws governing adsorption desorption and surface reactions. To estimate the parameters in a model equation, kinetic data unmasked by external and intraparticle mass transfer resistances have to be obtained. Kinetic data obtained at low conversions can be analysed by means of differential analysis. However, in complex reactions, at low conversions, only the main products are detected and a rigorous analysis of the data may not be possible. In such cases, data at high conversions have to be analysed by the integral method of analysis. In this case, parameters have to be estimated in differential equations which invariably involve numerical integrations. A comprehensive review on kinetic modelling has been presented by Froment and Hosten 49 .

Since catalyst B gave better yields of maleic anhydride, it has been chosen for kinetics and modelling. External and intraparticle mass transfer resistances have been eliminated as discussed in an earlier chapter (Chapter 5). The kinetic data have been treated by the integral method of analysis.

6.1 Kinetic Model:

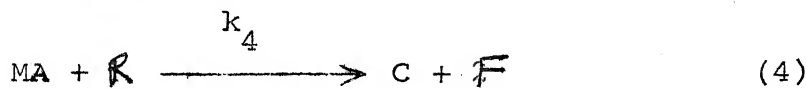
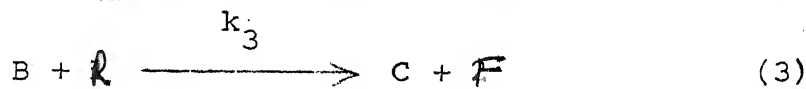
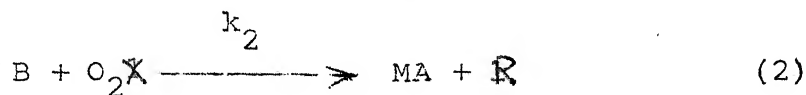
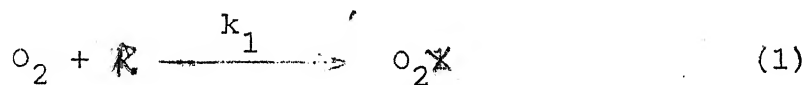
The selective oxidation reactions on oxide catalysts are assumed to follow redox mechanism proposed by Mars and Van Krevelen (40). In the case of n-butane oxidation on VPO catalysts, evidence in support of redox mechanism has been established as discussed in Chapter 2. In the following, a kinetic model based on the redox concept, but involving three types of active sites with different degrees of oxidation state has been presented.* The proposed reaction scheme is as follows:



The following individual reaction steps are considered to be taking place on the catalyst.

* An important characteristic of VPO system is the oxidation state of the vanadium ions. Several investigators reported that a mixture of +5, +4 and +3 oxidation states is usually present

on the catalyst-surface (13, 23, 33). Thus in the present development of the kinetic model, the presence of three oxidation states is assumed for catalyst sites. 58



in which

B is butane

MA is maleic anhydride

C is oxides of carbon.

R is a reduced site

F is a further reduced site

and O_2X is an oxidized site.

The reaction steps 2, 3, and 4 are in accordance with the experimental finding that increased W/F values lead to increase in selectivity of maleic anhydride. The concentration of n-butane decreases along the length of the reactor, i.e., decreases with increasing values of W/F. This results in an increased oxidation state of the catalyst towards the end of the reactor. And, the associated increase in selectivity can, in turn, be attributed to the higher oxidation state of the catalyst. Hence, the formation of

maleic anhydride was associated with the reaction between n-butane and the oxidized site O_2X , and the formation of carbon oxides with the reaction between butane/maleic anhydride and the reduced site R . The site F with greater degree of reduction does not participate in hydrocarbon oxidation, but only oxidizes to site R which in turn gets oxidized to site O_2X .

At steady state, the net rates of production of sites, O_2X , R and F are equal to zero.

From equations 1 to 5,

$$r_{O_2X} = k_1 p_O \cdot \theta_2 - k_2 p_B \cdot \theta_1 = 0 \quad (6)$$

$$r_2 = k_3 p_B \cdot \theta_2 + k_4 p_{MA} \theta_2 - k_5 (1 - \theta_1 - \theta_2) p_O = 0 \quad (7)$$

where

θ_1 - is the fraction of O_2X sites

θ_2 - is the fraction of R sites

and $(1 - \theta_1 - \theta_2)$ - is the fraction of F sites

and p_B , p_{MA} , p_O and p_C correspond to partial pressures of n-butane, maleic anhydride, oxygen and oxides of carbon respectively.

From eqn (6),

$$\theta_1 = \frac{k_1 p_O}{k_2 p_B} \theta_2 \quad (8)$$

By substituting (8) in (7);

$$r_2 = (k_3 p_B + k_4 p_{MA} + k_5 p_O) \cdot \theta_2 -$$

$$k_5 p_O \left(1 - \frac{k_1 p_O}{k_2 p_B} \cdot \theta_2 \right) = 0$$

from this, θ_2 can be expressed as

$$\theta_2 = \frac{k_5 p_O}{(k_3 p_B + k_4 p_{MA} + k_5 p_O + k_5 p_O \cdot \frac{k_1 p_O}{k_2 p_B})}$$

by rearranging;

$$\theta_2 = \frac{1}{\left(1 + \frac{k_1 p_O}{k_2 p_B} + \frac{k_3 p_B}{k_5 p_O} + \frac{k_4 p_{MA}}{k_5 p_O} \right)} \quad (9)$$

From Eqs (2) & (3); the rate of n-butane depletion can be written as

$$r_B = k_2 p_B \cdot \theta_1 + k_3 p_B \cdot \theta_2$$

substituting for θ_1 from (8);

$$\begin{aligned} r_B &= k_1 p_O \cdot \theta_2 + k_3 p_B \cdot \theta_2 \\ &= (k_1 p_O + k_3 p_B) \cdot \theta_2 \end{aligned}$$

substituting for θ_2 from (9);

$$r_B = \frac{k_1 p_O + k_3 p_B}{\left(1 + \frac{k_1 p_O}{k_2 p_B} + \frac{k_3 p_B}{k_5 p_O} + \frac{k_4 p_{MA}}{k_5 p_O} \right)} \quad (10)$$

From (2) & (4) the rate of maleic anhydride formation can be written as

$$r_{MA} = k_2 p_B \cdot \theta_1 - k_4 p_{MA} \cdot \theta_2$$

substituting for θ_1 from (8),

$$\begin{aligned} r_{MA} &= k_{1P_O} \cdot \theta_2 - k_{4P_{MA}} \theta_2 \\ &= (k_{1P_O} - k_{4P_{MA}}) \cdot \theta_2 \end{aligned}$$

substituting for θ_2 from (9),

$$r_{MA} = \frac{k_{1P_O} - k_{4P_{MA}}}{\left(1 + \frac{k_{1P_O}}{k_{2P_B}} + \frac{k_{3P_B}}{k_{5P_O}} + \frac{k_{4P_{MA}}}{k_{5P_O}} \right)} \quad (11)$$

And, from (3) & (4), the rate of formation of oxides of carbon can be written as

$$\begin{aligned} r_C &= k_{3P_B} \cdot \theta_2 + k_{4P_{MA}} \cdot \theta_2 \\ &= (k_{3P_B} + k_{4P_{MA}}) \cdot \theta_2 \end{aligned}$$

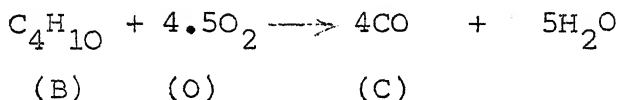
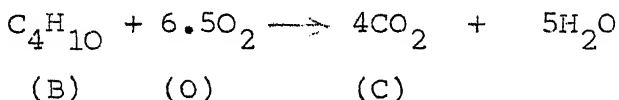
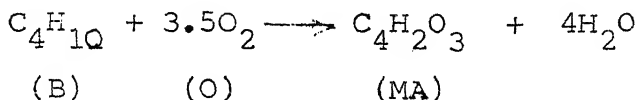
substituting for θ_2 from (9);

$$r_C = \frac{k_{3P_B} + k_{4P_{MA}}}{\left(1 + \frac{k_{1P_O}}{k_{2P_B}} + \frac{k_{3P_B}}{k_{5P_O}} + \frac{k_{4P_{MA}}}{k_{5P_O}} \right)} \quad (12)$$

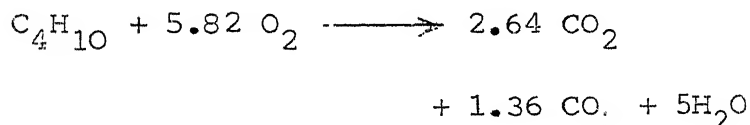
The partial pressures in Equations (10), (11) and (12) can be expressed in terms of the conversion of n-butane (X) the yield of maleic anhydride (Y), and the yield of carbon oxides (Z) as follows:

$$\begin{aligned} p_B &= p_B^O (1 - X) \\ p_{MA} &= p_B^O Y \\ p_C &= 4.0 p_B^O Z \end{aligned} \quad (13)$$

where p_B^O is the partial pressure of butane in the feed. To express the partial pressure of oxygen in terms of X, Y and Z, the stoichiometry of the reactions involved is to be accounted:



Further, the ratio of the rates of formation of CO_2 and CO is fixed at 1.942 based on the experimental results. Hence, on the average, the reaction for carbon oxides formation can be written as under:



From the above stoichiometry, oxygen partial pressure can be written as

$$p_O = p_O^O - 3.5 p_{MA} - \frac{5.82}{4.0} p_C$$

where p_O^O is the partial pressure of oxygen in the feed.

Substituting for p_{MA} and p_C from Eqn 13,

$$p_O = p_O^O - 3.5 p_B^O Y - \frac{5.82}{4.0} \times 4.0 p_B^O Z$$

or

$$p_O = p_O^O - 3.5 p_B^O Y - 5.82 p_B^O Z \quad (14)$$

It should be noted that Equations (13) and (14) make use of the approximation that volume changes accompanying the reactions are negligible. This is valid since the partial pressure of n-butane in the feed is very low and a large amount of inert (nitrogen) is present in the feed.

The continuity equations for n-butane, maleic anhydride and carbon oxides for the case of isothermal fixed bed reactor are as follows:

$$\begin{aligned}\frac{dx}{dW/F_B^0} &= r_B (X, Y) \\ \frac{dy}{dW/F_B^0} &= r_{MA} (X, Y) \\ \frac{dz}{dW/F_B^0} &= r_C (X, Y, Z)\end{aligned}\quad (15)$$

The initial conditions are,

$$\begin{aligned}X &= 0 \\ Y &= 0 \\ Z &= 0\end{aligned}\quad \text{at } W/F_B^0 = 0$$

where

W = weight of the catalyst bed

F_B^0 = Inlet flow-rate of n-butane

In the above equations, r_B and r_{MA} are functions of only X and Y . Hence, the first two equations can be solved to get X and Y independent of the third equation. And, Z is simply given by

$$Z = X - Y$$

Consequently, the set of continuity equations are modified to

$$\begin{aligned}\frac{dx}{dW/F_B^O} &= r_B (X, Y) \\ \frac{dy}{dW/F_B^O} &= r_{MA} (X, Y) \\ Z &= X - Y\end{aligned}\quad (16)$$

The initial conditions are

$$\begin{aligned}X &= 0 \\ Y &= 0\end{aligned}\quad \text{at } W/F_B^O = 0$$

The above model equations - describing the relationships between the conversion of butane, yields of maleic anhydride and oxides of carbon and W/F_B^O - are a set of three simultaneous first order differential equations involving five parameters k_1, k_2, k_3, k_4 and k_5 .

6.2 Parameter Estimation

The set of model equations (16) can be solved with the given initial conditions by the fourth order Runge-Kutta method for a given set of parameter values. In vector notation, the solution is given by:

The system:

$$\bar{Y}' = f(X, \bar{Y}) ; \quad \bar{Y}(X_0) = C_0$$

The solution:

$$\bar{Y}_{n+1} = \bar{Y}_n + \frac{h}{6} (K_1 + 2K_2 + 2K_3 + K_4)$$

$$\bar{K}_1 = \bar{f}(x_n, \bar{Y}_n)$$

$$\bar{K}_2 = \bar{f}\left(x_n + \frac{h}{2}, \bar{Y}_n + \frac{h\bar{K}_1}{2}\right)$$

$$\bar{K}_3 = \bar{f}\left(x_n + \frac{h}{2}, \bar{Y}_n + \frac{h\bar{K}_2}{2}\right)$$

$$\bar{K}_4 = \bar{f}(x_{n+1}, \bar{Y}_n + h\bar{K}_3)$$

A detailed discussion on this topic is given in the book of Roberts (50)

For the estimation of parameters minimization of the following simple least squares criterion has been used

$$A = \sum_i \frac{(x_i - x_i)_{\text{meas calc}}^2}{\text{meas calc}} + \sum_i \frac{(y_i - y_i)_{\text{meas calc}}^2}{\text{meas calc}} + \sum_i \frac{(z_i - z_i)_{\text{meas calc}}^2}{\text{meas calc}}$$

The subscripts used are

i - for ith experiment

meas - for measure value

calc - for calculated value for a given set of parameter values.

For minimizing the least squares criterion, a non-linear least squares regression subroutine EO₄FCF taken from

NAG fortran subroutine package has been used. The integration of the model equations was performed by the subroutine RUNGE (fourth order Runge-Kutta method) developed exclusively for the purpose. The flow-chart describing the process of parameter estimation is shown in Fig 6.1.

The estimated values for the five parameters along with the sum of squares of residuals are given in Table 6.1. The Arrhenius plots of $\ln K$ vs $1/T$ are shown in Fig 6.2. The points for all the parameters fall on straight lines. The activation energies are calculated and presented in Table 6.2. The calculated activation energies are all positive. In view of the acceptable characteristics of the parameters, the model is taken to be a viable one.

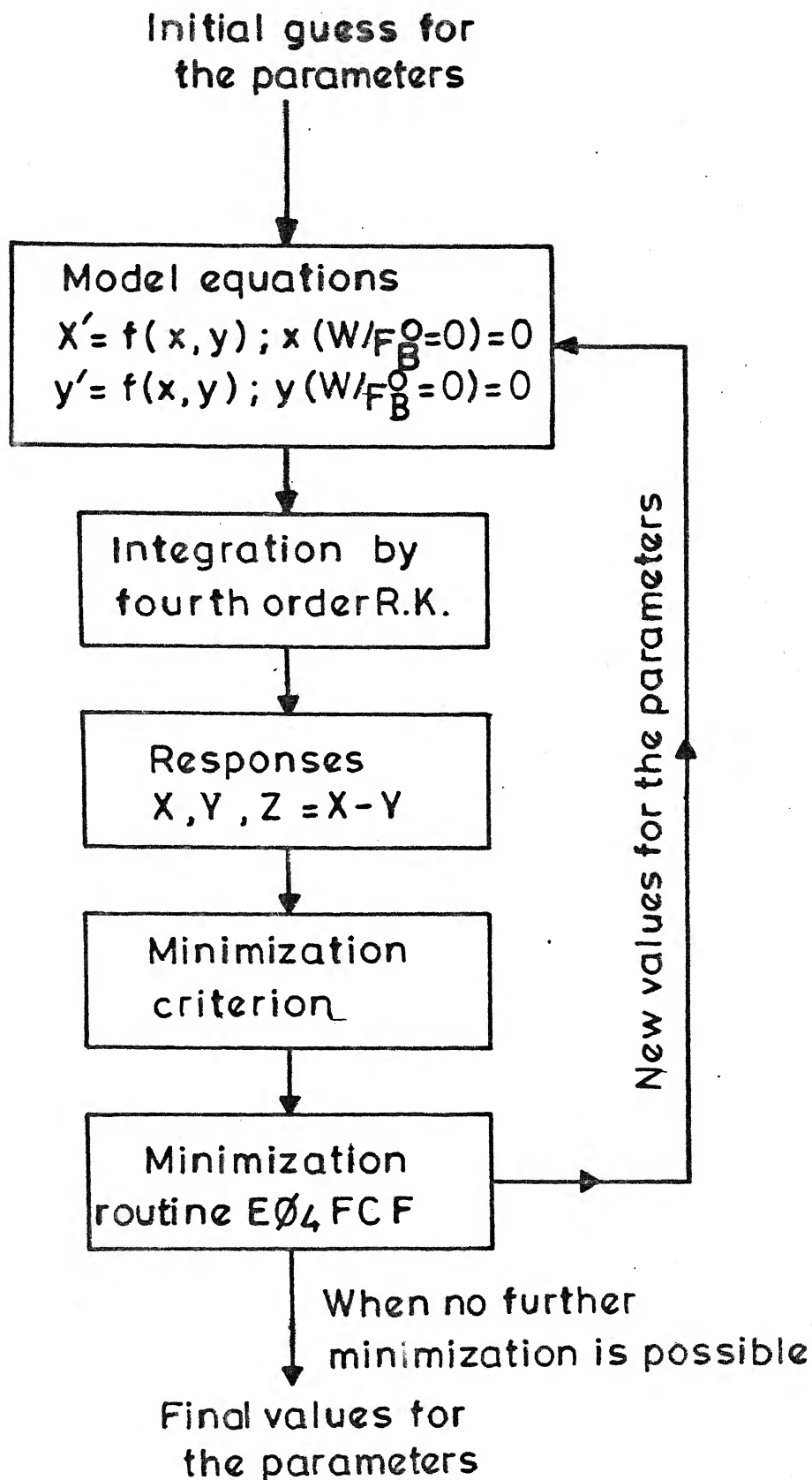


Fig. 6.1 - Flow chart for parameter estimation.

TABLE 6.1 ESTIMATED VALUES FOR THE PARAMETERS

Temperature, °C	k_1	k_2	k_3	k_4	k_5	R.S.S.
	mg mol/g s atm					
350	0.2748 E-1	0.4685 E-1	0.1437	0.4938	0.8653 E1	0.2250 E-2
375	0.2744 E0	0.5008 E-1	0.7327 E1	0.5262	0.3613 E2	0.3893 E-2
400	0.2007 E1	0.5141 E-1	0.2333 E3	0.5620	0.1267 E3	0.4806 E-2

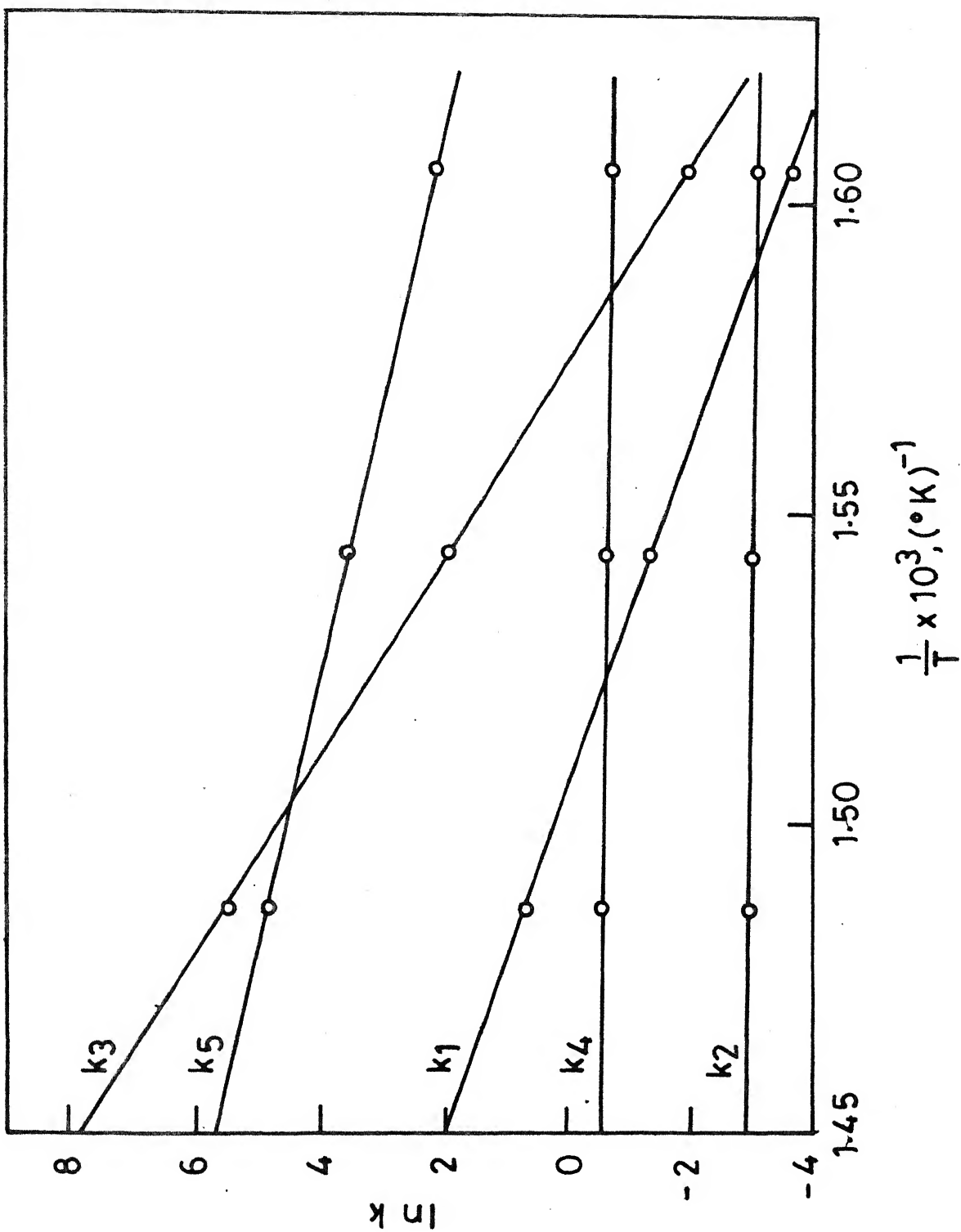


Fig. 6.2 - Arrhenius plots for rate constants.

TABLE 6.2 ACTIVATION ENERGIES FOR THE RATE CONSTANTS

Rate constants	Activation energy, E K cal/mol
<hr/>	
k_1	71.42
k_2	1.557
k_3	122.9
k_4	2.246
k_5	44.56

CHAPTER - 7

CONCLUSIONS AND RECOMMENDATIONS

The aim of the present work was to study the selective oxidation of n-butane to maleic anhydride using VPO catalysts. Accordingly catalyst A with a P/V ratio of 1.2/1.0 and catalyst B with a P/V/Fe ratio of 1.2/1.0/0.05 supported on silica gel were synthesised and examined for their activity and selectivity in n-butane oxidation to maleic anhydride using air. The catalysts were found to be thermally stable upto 500°C. XRD studies revealed the poorly crystalline nature of these catalysts, but both the catalysts showed two identical weak reflections indicating that the iron promotor had little effect on structural aspects. It is probable that iron modified the surface vanadium-oxygen bond strength.

Catalyst A was found to be more active. However, catalyst B was more selective for oxidation of n-butane to maleic anhydride. The selectivity to maleic anhydride decreased with an increase in n-butane concentration in the feed with both the catalysts. Catalyst B, despite being less active, gave better yield of maleic anhydride than catalyst A. For example, the yield of maleic anhydride on catalyst B was 29.8% compared to that on catalyst A of 23.73% at W/F = 9.0. The improved yields of maleic anhydride on

catalyst B may be attributed to the presence of iron which appears to improve the average valence of vanadium towards the optimum value by altering the surface energetics.

A kinetic model of n-butane oxidation on catalyst B has been carried out. A surface redox mechanism with three sites of different oxidation state were considered to take part in the redox cycles. The formation of maleic anhydride was associated with the sites of the highest oxidation state (V^{5+}) and the formation of carbon oxides was associated with the sites of intermediate oxidation state (V^{4+}). The proposed model constituting the five individual reaction steps fitted the experimental data very well.

The present study provides a reasonable understanding of an industrially important complex reaction using newly developed catalysts. The data are likely to be useful for commercial considerations.

Recommendations:

The following recommendations are made for future work:

1. Characterization of surface oxidation state of VPO catalysts during reaction conditions will elucidate the nature of active sites participating in n-butane oxidation to maleic anhydride. A study on these aspects is recommended.

2. The influence of promoters such as iron on VPO catalysts with P/V ratio close to unity offers scope for another interesting study.
3. Some of the industrial reactors for the oxidation of n-butane to maleic anhydride operate within the explosive limits of the reactants. It may be desirable to conduct a systematic study over a wide range of concentrations of the reactants.

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APPENDIX 1MODEL CALCULATION OF CONVERSION, YIELD
AND SELECTIVITYRun No. 85

Catalyst : B
 W/F : 9 g/(mg mol/s)
 F_{in} : 1125 cc/min
 Butane conc in
 feed, $C_{B,in}$: 0.6 mol%

Since low concentrations of butane in feed are used, the volume changes associated with the reaction may be neglected.

$$F_{in} = F_{out} = F$$

Composition of products (mol %)

Butane, $C_{B,out}$: 0.295
MA , C_{MA}	: 0.191
CO ₂ , C_{CO_2}	: 0.302
CO , C_{CO}	: 0.155

Results:

Mol of butane converted

$$\begin{aligned}
 &= (F_{in} C_{B,in} - F_{out} C_{B,out}) \\
 &= F(C_{B,in} - C_{B,out})
 \end{aligned}$$

Mol of butane fed

$$= F_{in} C_{B,in}$$

$$= F C_{B,in}$$

Mol of MA formed

$$= F_{out} C_{MA}$$

$$= F C_{MA}$$

$$\begin{aligned} \text{Conversion of butane, \%} &= \frac{F(C_{B,in} - C_{B,out})}{F C_{B,in}} \times 100 \\ &= \frac{0.6 - 0.295}{0.6} \times 100 \end{aligned}$$

$$= 50.833\%$$

$$\begin{aligned} \text{Yield of MA, \%} &= \frac{F C_{MA}}{F C_{B,in}} \times 100 \\ &= \frac{0.191}{0.6} \times 100 \end{aligned}$$

$$= 31.833\%$$

Selectivity of MA, %

$$\begin{aligned} &= \frac{F C_{MA}}{F (C_{B,in} - C_{B,out})} \times 100 \\ &= \frac{0.191}{0.6 - 0.295} \times 100 \end{aligned}$$

$$= 62.62\%$$

APPENDIX - 2EXPERIMENTAL DATA AND RESULTS

<u>RUN NO</u>	1	2	3	4	5
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RUN CONDITIONS

CATALYST NO.	0	0	0	0	0
TEMPERATURE, *C	375.0	375.0	300.0	300.0	300.0
W/F, G/(MGMOL/S)	3.0	4.5	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

P00	.208	.208	.208	.208	.208
PB0	.010	.010	.006	.008	.010

PRODUCT COMP, ATM

PB	.003860	.002790	.005800	.006560	.009170
PMA	.000839	.001164	.000060	.000164	.000340
PCO2	.013400	.015700	.000370	.000920	.001610
PCO	.007840	.008470	.000190	.000440	.000790

RESULTS

CONV OF BUTANE, %	61.40	72.10	3.33	5.50	8.30
YIELD OF MA, %	8.39	11.64	1.00	2.05	3.40
SELEC OF MA, %	13.66	16.14	30.00	37.27	40.96

NO.--CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO	6	7	8	9	10
<u>RUN CONDITIONS</u>					
CATALYST NO.	0	0	0	0	0
TEMPERATURE, °C	300.0	325.0	325.0	325.0	325.0
W/F, G(MGMOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.012	.006	.008	.010	.012
<u>PRODUCT COMP, ATM</u>					
PB	.010240	.005560	.006890	.007540	.008470
PMA	.000430	.000182	.000323	.000670	.000850
PCO ₂	.003710	.000850	.002370	.005120	.007420
PCO	.001810	.000430	.001150	.002480	.003620
<u>RESULTS</u>					
CONV OF BUTANE, %	14.67	7.33	13.88	24.60	29.42
YIELD OF MA, %	3.58	3.03	4.04	6.70	7.08
SELEC OF MA, %	24.43	41.36	29.10	27.24	24.08

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO	11	12	13	14	15
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RUN CONDITIONS

CATALYST NO.	0	0	0	0	0
TEMPERATURE, *C	350.0	350.0	350.0	350.0	375.0
W/F, G/(MG MOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.006	.008	.010	.012	.006

PRODUCT COMP, ATM

PB	.004870	.004840	.005080	.003650	.003950
PMA	.000364	.000850	.001050	.001330	.000640
PCO ₂	.002350	.006530	.010770	.019100	.004100
PCO	.001010	.003070	.005230	.009220	.001900

RESULTS

CONV OF BUTANE, %	18.83	39.50	49.20	69.58	34.17
YIELD OF MA, %	6.07	10.62	10.50	11.08	10.67
SELEC OF MA, %	32.21	26.90	21.34	15.93	31.22

NO.--CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	16	17	18	19	20
<u>RUN CONDITIONS</u>					
CATALYST NO.	0	0	0	0	0
TEMPERATURE, °C	375.0	375.0	375.0	400.0	400.0
W/F, G/(MG MOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
P00	.208	.208	.208	.208	.208
PB0	.008	.010	.012	.006	.008
<u>PRODUCT COMP, ATM</u>					
PB	.002470	.002030	.000660	.002120	.000860
PMA	.001230	.001530	.001690	.000970	.001230
PCO2	.011850	.017460	.026000	.008200	.016000
PCO	.005750	.008540	.012880	.003800	.008000
<u>RESULTS</u>					
CONV OF BUTANE, %	69.13	79.70	94.50	64.67	89.25
YIELD OF MA, %	15.37	15.30	14.08	16.17	15.37
SELEC OF MA, %	22.24	19.20	14.90	25.00	17.23
NO.- CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"					

Appendix 2 (contd)

RUN NO.	21	22	23	24	25
<u>RUN CONDITIONS</u>					
CATALYST NO.	0	0	0	0	1
TEMPERATURE, *C	400.0	400.0	375.0	375.0	350.0
W/F, G/(MG MOL/S)	6.0	6.0	7.5	9.0	3.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.010	.012	.010	.010	.006
<u>PRODUCT COMP, ATM</u>					
PB	.000550	.000000	.001190	.000546	.005140
PMA	.001470	.001590	.001926	.002373	.000734
PCO2	.021900	.028000	.017760	.018500	.000340
PCO	.010500	.013700	.009780	.009830	.000177
<u>RESULTS</u>					
CONV OF BUTANE, %	94.50	100.00	88.10	94.54	14.33
YIELD OF MA, %	14.70	13.25	19.26	23.73	12.23
SELEC OF MA, %	15.56	13.25	21.86	25.10	85.35

NO.--CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	26	27	28	29	30
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	350.0	350.0	350.0	375.0	375.0
W/F, G/(MG MOL/S)	3.0	3.0	3.0	3.0	3.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.008	.010	.012	.006	.008
<u>PRODUCT COMP, ATM</u>					
PB	.006870	.008560	.009920	.004650	.006070
PMA	.000911	.001110	.001520	.000797	.001000
PCO ₂	.000568	.000870	.001490	.001470	.002450
PCO	.000290	.000449	.000767	.000757	.001260
<u>RESULTS</u>					
CONV OF BUTANE, %	14.13	14.40	17.33	22.50	24.13
YIELD OF MA, %	11.39	11.10	12.67	13.28	12.50
SELEC OF MA, %	80.62	77.08	73.08	59.04	51.81

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO	31	32	33	34	35
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	375.0	375.0	400.0	400.0	400.0
W/F, G/(MG MOL/S)	3.0	3.0	3.0	3.0	3.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.010	.012	.006	.008	.010
<u>PRODUCT COMP, ATM</u>					
PB	.007350	.008040	.003410	.004160	.004670
PMA	.001230	.001680	.000723	.000876	.001040
PCO2	.003750	.006020	.004940	.007830	.011320
PCO	.001930	.003100	.002540	.004030	.005830
<u>RESULTS</u>					
CONV OF BUTANE, %	26.50	33.00	43.17	48.00	53.30
YIELD OF MA, %	12.30	14.00	12.05	10.95	10.40
SELEC OF MA, %	46.42	42.42	27.92	22.81	19.51

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO	36	37	38	39	40
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, °C	400.0	350.0	350.0	350.0	350.0
W/F, G/(MGMOL/S)	3.0	4.5	4.5	4.5	4.5
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.012	.006	.008	.010	.012

PRODUCT COMP, ATM

PB	.004450	.004810	.006280	.007930	.009460
PMA	.001320	.001000	.001370	.001570	.001820
PCO2	.016430	.000500	.000930	.001330	.001880
PCO	.008460	.000258	.000480	.000686	.000968

RESULTS

CONV OF BUTANE, %	62.92	19.83	21.50	20.70	21.17
YIELD OF MA, %	11.00	16.67	17.12	15.70	15.17
SELEC OF MA, %	17.48	84.03	79.65	75.85	71.65

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	41	42	43	44	45
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	375.0	375.0	375.0	375.0	400.0
W/F, G/ (MG MOL/S)	4.5	4.5	4.5	4.5	4.5
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.006	.008	.010	.012	.006

PRODUCT COMP, ATM

PB	.004190	.005210	.006390	.007340	.002810
PMA	.001080	.001480	.001710	.002010	.000935
PCO ₂	.001920	.003450	.005000	.007000	.005960
PCO	.000989	.001780	.002580	.003610	.003070

RESULTS

CONV OF BUTANE, %	30.17	34.88	36.10	38.83	53.17
YIELD OF MA, %	18.00	18.50	17.10	16.75	15.58
SELEC OF MA, %	59.67	53.05	47.37	43.13	29.31

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	46	47	48	49	50
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	400.0	400.0	400.0	300.0	300.0
W/F, G/(MG MOL/S)	4.5	4.5	4.5	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.008	.010	.012	.006	.008

PRODUCT COMP, ATM

PB	.003110	.003550	.003750	.005740	.007530
PMA	.001200	.001350	.001510	.000254	.000464
PCO ₂	.009740	.013500	.017800	.000000	.000016
PCO	.005020	.006940	.009170	.000000	.000008

RESULTS

CONV OF BUTANE, %	61.13	64.50	68.75	4.33	5.88
YIELD OF MA, %	15.00	13.50	12.58	4.23	5.80
SELEC OF MA, %	24.54	20.93	18.30	97.69	98.72

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd.)

RUN NO.	51	52	53	54	55
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	300.0	300.0	325.0	325.0	325.0
W/F, G/(MG MOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.010	.012	.006	.008	.010
<u>PRODUCT COMP, ATM</u>					
PB	.009280	.010940	.005330	.007010	.008510
PMA	.000709	.001030	.000638	.000916	.001360
PCO2	.000029	.000081	.000085	.000197	.000348
PCO	.000015	.000039	.000044	.000099	.000172
<u>RESULTS</u>					
CONV OF BUTANE, %	7.20	8.83	11.17	12.38	14.90
YIELD OF MA, %	7.09	8.58	10.63	11.45	13.60
SELEC OF MA, %	98.47	97.17	95.22	92.53	91.28

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	56	57	58	59	60
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	325.0	350.0	350.0	350.0	350.0
W/F, G/(MG MOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.012	.006	.008	.010	.012
<u>PRODUCT COMP, ATM</u>					
PB	.009930	.004400	.005920	.007350	.008620
PMA	.001850	.001330	.001640	.001970	.002370
PCO2	.000591	.000713	.001180	.001800	.002660
PCO	.000289	.000370	.000610	.000930	.001370
<u>RESULTS</u>					
CONV OF BUTANE, %	17.25	26.67	26.00	26.50	28.17
YIELD OF MA, %	15.42	22.17	20.50	19.70	19.75
SELEC OF MA, %	89.37	83.12	78.85	74.34	70.12

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	61	62	63	64	65
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, °C	375.0	375.0	375.0	375.0	400.0
W/F, G/(MG MOL/S)	6.0	6.0	6.0	6.0	6.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.006	.008	.010	.012	.006

PRODUCT COMP, ATM

PB	.003670	.004730	.005600	.006190	.002240
PMA	.001420	.001760	.002140	.002570	.001160
PCO ₂	.002400	.003980	.005980	.008550	.006860
PCO	.001230	.002050	.003080	.004400	.003530

RESULTS

CONV OF BUTANE, %	38.83	40.88	44.00	48.42	62.67
YIELD OF MA, %	23.67	22.00	21.40	21.42	19.33
SELEC OF MA, %	60.94	53.82	48.64	44.23	30.85

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	66	67	68	69	70
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	400.0	400.0	400.0	350.0	350.0
W/F, G/(MGMOL/S)	6.0	6.0	6.0	7.5	7.5
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.008	.010	.012	.006	.008
<u>PRODUCT COMP, ATM</u>					
PB	.002620	.002810	.002780	.004120	.005410
PMA	.001380	.001580	.001800	.001540	.002000
PCO2	.010600	.014800	.019500	.000870	.001540
PCO	.005440	.007620	.010000	.000450	.000790
<u>RESULTS</u>					
CONV OF BUTANE, %	67.25	71.90	76.82	31.33	32.38
YIELD OF MA, %	17.25	15.80	15.00	25.67	25.00
SELEC OF MA, %	25.65	21.97	19.52	81.91	77.22

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	71	72	73	74	75
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	350.0	350.0	375.0	375.0	375.0
W/F, G/(MG MOL/S)	7.5	7.5	7.5	7.5	7.5
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.010	.012	.006	.008	.010

PRODUCT COMP, ATM

PB	.006810	.007850	.003330	.004110	.004930
PMA	.002330	.002840	.001640	.002140	.002500
PCO2	.002260	.003440	.002700	.004620	.006760
PCO	.001160	.001770	.001390	.002380	.003480

RESULTS

CONV OF BUTANE, %	31.90	34.58	44.50	48.63	50.70
YIELD OF MA, %	23.30	23.67	27.33	26.75	25.00
SELEC OF MA, %	73.04	68.43	61.42	55.01	49.31

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (Contd)

RUN NO.	76.	77	78	79	80
<u>RUN CONDITIONS</u>					
CATALYST NO.	1	1	1	1	1
TEMPERATURE, *C	375.0	400.0	400.0	400.0	400.0
W/F, G/(MGMOL/S)	7.5	7.5	7.5	7.5	7.5
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0
<u>FEED COMP, ATM</u>					
POO	.208	.208	.208	.208	.208
PBO	.012	.006	.008	.010	.012
<u>PRODUCT COMP, ATM</u>					
PB	.005270	.001920	.002090	.002290	.002160
PMA	.003050	.001310	.001590	.001780	.002020
PCO2	.009710	.007330	.011400	.015700	.020600
PCO	.005000	.003770	.005870	.008060	.010600
<u>RESULTS</u>					
CONV OF BUTANE, %	56.08	68.00	73.88	77.10	82.00
YIELD OF MA, %	25.42	21.83	19.87	17.80	16.83
SELEC OF MA, %	45.32	32.11	26.90	23.09	20.53

NO.-CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN NO.	81	82	83	84	85
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RUN CONDITIONS

CATALYST NO.	1	1	1	1	1
TEMPERATURE, °C	350.0	350.0	350.0	350.0	375.0
W/F, G/(MGMOL/S)	9.0	9.0	9.0	9.0	9.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP, ATM

POO	.208	.208	.208	.208	.208
PBO	.006	.008	.010	.012	.006

PRODUCT COMP, ATM

PB	.003780	.004950	.006080	.007500	.002950
PMA	.001810	.002320	.002800	.003050	.001910
PCO2	.001080	.001900	.002940	.003820	.003020
PCO	.000560	.000980	.001520	.001970	.001550

RESULTS

CONV OF BUTANE, %	37.00	38.13	39.20	37.50	50.83
YIELD OFMA, %	30.17	29.00	28.00	25.42	31.83
SELEC OF MA, %	81.53	76.07	71.43	67.78	62.62

NO.--CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

Run No.	86	87	88	89	90
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RUN CONDITIONS

CATALYST No.	1	1	1	1	1
TEMPERATURE, °C	375.0	375.0	375.0	400.0	400.0
W/F, G (MGMOL/S)	9.0	9.0	9.0	9.0	9.0
F-IN, CC/MIN	1125.0	1125.0	1125.0	1125.0	1125.0

FEED COMP.ATM

PDO	.208	.208	.208	.208	.208
PBO	.008	.010	.012	.006	.008

PRODUCT COMP.ATM

PB	.003600	.004120	.004880	.001590	.001710
PMA	.002460	.002980	.003260	.001470	.001760
PCO2	.005120	.007650	.010100	.007800	.012000
PCO	.002630	.003940	.005240	.004000	.006150

RESULTS

CONV OF BUTANE, %	55.00	58.80	59.33	73.50	78.63
YIELD OF MA, %	30.75	29.80	27.17	24.50	22.00
SELEC OF MA, %	55.91	50.68	45.79	33.33	27.98

No. CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"

Appendix 2 (contd)

RUN No.	91	92
<u>RUN CONDITIONS</u>		
CATALYST NO.	1	1
TEMPERATURE, °C	400.0	400.0
W/F, G./ (MGMOL/S)	9.0	9.0
F-IN, CC/MIN	1125.0	1125.0
<u>FEED COMP, ATM</u>		
PDO	.208	.208
PBO	.010	.012
<u>PRODUCT COMP, ATM</u>		
PB	.001750	.001930
PMA	.001750	.001930
PMA	.002000	.002120
PCO2	.016500	.021000
PCO	.008500	.010800
<u>RESULTS</u>		
CONV OF BUTANE, %	82.50	83.92
YIELD OF MA, %	20.00	17.67
SELEC OF MA, %	24.24	21.05

NO. CATALYST = 0 IS "CAT A" AND = 1 IS "CAT B"